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Inorganic Chemistry

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PREFACE

The volumes of the International Library of Technology are made up of Instruction Papers, or Sections, comprising the various courses of instruction for students of the International Correspondence Schools. The original manuscripts are prepared by persons thoroughly qualified both technically and by experience to write with authority, and in many cases they are regularly employed elsewhere in practical work as experts. The manuscripts are then carefully edited to make them suitable for correspondence instruction. The Instruction Papers are written clearly and in the simplest language possible, so as to make them readily understood by all students. Necessary technical expressions are clearly explained when introduced.

The great majority of our students wish to prepare themselves for advancement in their vocations or to qualify for more congenial occupations. Usually they are employed and able to devote only a few hours a day to study. Therefore every effort must be made to give them practical and accurate information in clear and concise form and to make this information include all of the essentials but none of the non-essentials. To make the text clear, illustrations are used freely. These illustrations are especially made by our own Illustrating Department in order to adapt them fully to the requirements of the text.

In the table of contents that immediately follows are given the titles of the Sections included in this volume, and under each title are listed the main topics discussed. At the end of the volume will be found a complete index, so that any subject treated can be quickly found.

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INORGANIC CHEMISTRY
(PART 1)

CHEMICAL THEORY, DEFINITIONS, AND LAWS

GENERAL INTRODUCTION

1. History of Chemistry.—The history of chemistry from its obscure beginning to the present time, when it has become indispensable to mankind, is an interesting one. To learn how chemistry developed to its present important position, one should know something about the various theories and about the different men intimately connected with the development of the science.

The desire to change common metals like lead into gold gave rise to a class of men known as alchemists. To them is due the foundation of what has since developed into modern chemical science and industry, without which human progress would have been seriously retarded. It was not, however, until chemists began to study facts in relation to one another that certain fundamental laws were discovered and chemistry became a real science.

It was supposed in early times that earth, fire, water, and air were four elements that constituted everything in the universe, and it was not until the latter part of the 18th Century that Priestley and Cavendish in England, Scheele in Sweden, and Lavoisier in France proved that water is made up of hydrogen and oxygen and that air consists chiefly of nitrogen and oxygen. These great discoveries have formed

the groundwork for all chemical investigations down to the present time.

2. Priestley and the Discovery of Oxygen.—Priestley, whose chief discovery was oxygen gas, was a clergyman who became interested in the study of gases through watching the gases formed on the surface of fermented liquids in a brewery near his home in Birmingham, England. Mistreatment by his neighbors on account of his independent religious views finally resulted in his immigration to America. He spent the balance of his days in Northumberland, Pennsylvania. His discovery of oxygen was one of the most important of all advances made in the history of chemistry.

3. Scheele and His Discoveries.—Scheele, a poor druggist of Stockholm, Sweden, made a larger number of discoveries than any other chemist of early times. His two most important ones are oxygen and chlorine; the former gas was found independently of Priestley though, by curious coincidence, in the same year, 1774. Chlorine is of great commercial importance as a disinfectant, bleaching agent, solvent in gold metallurgy, and reagent in the manufacture of dyes and medicines.

4. Cavendish and the Fixation of Nitrogen.—Cavendish undertook chemical investigation as a hobby, for he was wealthy and did not have to earn a living. He contributed to the advancement of chemistry a process that is today the basis of an important industry, the extraction of nitrogen from the air. He showed that oxygen and nitrogen combine when the electric spark is passed through air and that these elements with water form nitric acid, a chemical which is indispensable in the manufacture of fertilizers and explosives. The industry based upon this discovery of Cavendish is daily becoming more important, as it is possible, that because of it mankind can become commercially independent of the one hitherto available important source of nitrates, Chile, South America.

5. Lavoisier and the Phlogiston Theory.—Lavoisier, one of the most brilliant chemists of all times, has the honor of

being the first scientist to recognize clearly the importance of the discovery of oxygen; in fact, his work was so valuable to chemistry that he has been called by some the founder of the science. We owe our present knowledge of the relation of oxygen to combustion, or burning, to him, for previous to his time the phlogiston theory prevailed. This theory advanced the idea that burning was due to the escape of an imaginary subtle substance called *phlogiston;* that those materials which were combustible contained phlogiston and that those materials which did not burn did not contain it. This theory had become so firmly fixed among scientists during the 100 years it prevailed that even the convincing work of Lavoisier did not completely dispel it.

6. **Dalton and the Atomic Hypothesis.**—Dalton, a poor English school teacher, contributed to chemistry the atomic theory, a vehicle by means of which chemists are able to convey their theories of chemical changes in a simple way. Today this theory controls the activities of chemical enterprise and, though not yet perfected, forms an indispensable part of chemical knowledge.

7. **Berzelius and Analytical Chemistry.**—Berzelius, a Swedish investigator, in his efforts to verify the atomic theory, dedicated to chemical advancement many important improvements in analytical methods. The laboratory in which he experimented showed that success in chemistry is largely dependent on the man and not altogether upon the things with which he works. His laboratory contained a table, a cook stove, a tub of water, and some bottles. His only assistant was Anna, the cook, who, in addition to helping him, had to prepare the meals and take care of the household. The example set by Berzelius should serve as an inspiration to any one who is learning chemistry at home and making the necessary tests in a home laboratory.

8. **Liebig and Public Laboratories.**—Until the 19th Century, all laboratories were private, for there were no places to which a person could go for instruction and guidance in chemical endeavors; neither was there any system whereby a

student could receive the necessary instruction in his home. Liebig, a German scientist of considerable prominence during that period, is largely responsible for the establishment of the first public chemical laboratory. It was located at the University of Giessen. His widespread influence as a chemist and educator attracted students from all parts of the world and enabled many men to fit themselves for work along chemical lines. Liebig is also the founder of our present system of determining the relative value of chemical research to industry. Companies of industrial importance are today calling on chemically-trained men to help solve their many manufacturing and economic problems; signs of the times point to an even greater future demand for men who have the chemical knowledge necessary to aid companies in their industrial endeavors. Liebig is an inspiration to the many men who seek ways and means of conserving and using to the best advantage the resources of the world.

9. The Discovery of Wöhler.—Previous to 1828 chemists supposed that organic compounds were obtained only from living matter and that they could not be prepared artificially in the laboratory. Wöhler, in that year, succeeded in making urea, an excretion of certain animal organisms, from ammonium cyanate, which is an entirely different substance. This pioneer work led to the discovery that many other organic substances could be made by artificial means. Many of the most important organic substances used are now being artificially produced in factories and laboratories. The discovery of Wöhler was one of the most important contributions to the advancement of chemistry.

10. Recent Progress in Chemistry.—There were, of course, many other important discoveries that affected the progress of chemical knowledge greatly, but those mentioned are the fundamental ones upon which modern investigations and endeavors depend.

At present, chemistry has advanced to a position of prime importance and the theory of chemistry is so exact that one can now undertake to accomplish various tasks with some

degree of certainty and reasonable expectation of success. The opening of the European war in 1914 found America with certain great resources undeveloped and unused, for previous to this year it was cheaper to order from Europe whatever dyes, glassware, fertilizers, etc., that were needed. The cutting off of this source of supply meant that the natural resources had to be developed without delay, for demands were pressing. Fortunately, chemistry had advanced sufficiently to overcome the many problems that arose during this period of development, and today, thanks to men who are chemically trained, American-made goods such as potash products, glassware, porcelain ware, stoneware, coal-tar dyes, special metallurgical materials, drugs, and photographic materials, can be obtained. Though some of the industries making these products may be only temporary in character, the wonderful development of them from mere ideas shows that chemical progress made since the days of the alchemist has placed the science and profession in a position where it will always play an important role in supplying the needs and in conserving the resources of mankind.

COMPOSITION AND DIVISION OF MATTER

11. Matter.—Each of the terms used in chemistry has a distinct and definite meaning that must be understood by any one who wishes to study the laws and principles upon which the application of chemistry is based. Everything is subject to some kind of change that will alter its appearance, form, or chemical nature. Trees, grass, air, water—in fact, all kinds of things—have two points of similarity. They all have weight and occupy space, and are called *matter*.

12. Properties of Matter.—A study of the different kinds of matter reveals the fact that each variety has peculiarities or characteristics by which it can be recognized and identified. For example, one may recognize a white substance as sugar, if it is white and sweet. Qualities by which matter can be identified are called properties of matter. Whiteness and sweetness are properties of sugar. In general, color, taste, and

touch are some of the properties of matter that enable one to distinguish different things.

The separate particles of crystallized sugar differ from those of powdered sugar in size and shape, but they resemble each other in color, taste, and touch. One can change crystallized sugar to powdered sugar by breaking up the former, thereby altering the size and shape of its particles. It is obvious, therefore, that properties such as size and shape can be changed without destroying the nature of the substance, while others are constant and specific properties of a substance which cannot be changed without altering its chemical nature. To change the color and sweetness of sugar, one must change the sugar to something else that is not sugar. Properties that can be changed without altering the chemical nature of the substance are called conditional properties, and properties that cannot be changed without altering the chemical nature of the substance are called specific properties.

From the foregoing, it is apparent that matter has characteristics that affect the senses in different ways. The color, size, and shape of matter have definite effects on sight; its odor on smell; its sweetness, sourness, and bitterness on taste; and its stickiness and smoothness on touch. These characteristics are called properties of matter.

13. Substances.—It is necessary to apply the term substance properly, for it is used frequently in the study of chemistry. For example, sugar with its sweetness and whiteness, is a substance, for it retains these specific properties no matter how much its conditional properties, size and shape, may vary.

Steel is a substance, for it retains its specific properties, hardness, strength, luster, and color, no matter how much its conditional properties, shape and size, may be altered. It still remains the substance steel, even if made into a needle, rail, or axle.

Wood is a substance, since it retains its specific properties, its fibrous and fairly hard nature, no matter whether its form be that of a table, chair, or desk.

Matter, such as sugar, steel, or wood, retains its specific properties as long as its chemical composition remains the same. If one changes the chemical composition of sugar, the resultant product is no longer sugar, but a new substance possessing an entirely new set of specific properties. Hence, a substance may be considered as any form of matter that has distinct specific properties.

14. Chemical and Physical Changes.—There is a distinction between changes that are chemical and those that are physical. It is well to learn this distinction, for the whole of the science of chemistry is based on changes of some sort. If sugar is broken into smaller pieces, it still remains sugar, for only the conditional properties, shape and size, have been altered. If, on the other hand, heat is applied to the sugar, it soon darkens, loses its whiteness and sweetness and becomes something other than sugar, for the specific properties, taste and color, of the substance sugar have disappeared. In other words, the chemical composition of the substance sugar has been altered. The first change, in which sugar retains its chemical composition, is called a physical change, while the second change, in which the substance sugar is changed to an entirely different substance by altering its chemical composition, is called a chemical change. Hence, changes that do not affect the composition of substances are called physical changes, and changes in which substances disappear and something else is formed in their place are called chemical changes.

A lump of coal can be broken up and powdered finely without its color and hardness being destroyed; it still remains coal, even though changed in size and shape. This is a physical change. If, however, coal is burned, it loses its color and hardness, gives off a gas, and leaves a gray residue, called ash. The substance coal when burned loses its specific properties by which it is identified and forms new substances possessing other specific properties. This is a chemical change. It is apparent, therefore, that the specific properties of a substance are destroyed in a chemical change and are not affected in a physical change. In other words, a substance

is not changed chemically as long as it retains its specific properties, and it is changed chemically when its specific properties disappear.

15. Physics and Chemistry.—Like all other sciences, physics and chemistry treat of definite subjects. **Physics** is that branch of science that deals with changes that do not affect the composition of substances. **Chemistry** is that branch of science that treats of changes that affect the composition of substances. It should be borne in mind, however, that chemical changes, as will be shown later, are always accompanied by physical ones, and it is almost impossible to study chemistry without keeping in mind the physical principles involved.

16. Organic and Inorganic Chemistry.—Chemistry is a broad science, for it treats of every change in the universe in which the composition of matter is involved. In a general way it may be stated that the two classes of substances recognized are those that contain the element carbon and those that do not contain it. The portion of chemistry that deals with substances containing carbon is called organic chemistry, and the portion that treats of substances other than those containing carbon is called inorganic chemistry. Some carbon compounds such as carbon dioxide, carbon monoxide, carbonates, and carbon disulphide, are exceptions to these definitions and are described in both divisions of chemistry.

17. Mass.—It has been shown that everything in nature that has weight and occupies space is known as matter, but no reference has been made to the composition of the substances that make up the different kinds of matter, and as this subject is both interesting and important, it should be given careful thought.

Consider, as an example, common rock salt. A lump of this substance affects the senses in a definite way, for one can note its shape and size by sight, its saltiness by taste, its lack of odor by smell, and its sharp edges by touch. This lump of salt is a mass of matter; that is, a combination of matter appreciable to the senses.

18. Divisions of Matter.—The question naturally arises as to what constitutes a mass of matter, as to whether it is made up of particles, and, if so, as to how finely a mass can be divided by physical means without destroying its specific properties. Formerly, the view was held that all substances were continuous and there was no limit, theoretically, beyond which division could not be carried. This view has been discarded for the view, now accepted, that substances are composed of extremely small separate particles and that subdivision by physical means can be repeated only until these minute particles are reached. Furthermore, these minute particles called molecules are conceived as having the same specific properties as the substances from which they are obtained. It should be borne in mind that the molecule is merely a conception, for it has never been actually isolated. A **molecule** then, may be defined as the smallest particle of matter in which the original properties of the substance are retained.

19. Hypothesis Defined.—The foregoing conception of molecules is known as the molecular hypothesis and is an excellent example of the line of reasoning often followed by scientists in their efforts to arrive at scientific truths. It is important, therefore, to understand the meaning of the term hypothesis at this point. Scientists note the various changes that take place, study them in detail, and seek to determine the causes for them. If no definite explanation results from their investigations, they proceed to imagine one, and then either prove or disprove it by tests. This imaginary explanation is called a hypothesis. The molecular hypothesis is today accepted as true, for tests all seem to verify and none seem to disprove it.

20. Molecules and Atoms.—Consider again the lump, or mass, of salt. Theoretically, but not actually, this mass can be subdivided repeatedly until an individual molecule of salt is obtained. If one were able to study this molecule of salt he would note that it shows the same specific properties as the mass of salt; it has the same taste and no apparent odor. The molecule of salt differs from the mass only in conditional prop-

erties such as size and shape; chemically, both the mass and molecule are the same, for the changes so far made are physical.

One naturally wonders whether the molecule can be divided further. From the foregoing discussion, it is obvious that the molecule cannot be divided by physical means, since a molecule is the smallest particle of a substance that can be obtained by physical means. There remain, however, chemical means by which division can be effected.

The atomic hypothesis, first advanced by Dalton, conceives the idea that molecules consist of atoms, particles that can be obtained, theoretically, by chemical means. Consider a molecule of salt. This substance has been found by experiment to contain two simple substances, sodium and chlorine, in chemical combination. Both the mass and molecule of salt have the chemical name sodium chloride. The elementary particles sodium and chlorine, of which a molecule of salt is made up, are called atoms and can be obtained from a molecule of sodium chloride only by chemical means. An **atom** is the smallest particle of matter that has yet been obtained by chemical means; but recent investigations have shown that it is not an indivisible unit of matter. The atom is taken as the unit of chemical changes. To illustrate the minute size of a molecule, it has been estimated that a molecule has a diameter of but a few ten-millionths of an inch.

21. Difference Between Chemical and Physical Changes.—The ultimate divisions of matter serve as the basis for simple definitions of chemical and physical changes. A physical change, as has been shown, can produce a molecule, but cannot affect its internal condition in any way, while a chemical change can act on a molecule to produce a change within it. Therefore, a **physical change** is one that does not affect a molecule and a **chemical change** is one that takes place within a molecule.

22. Electrons.—The atom is the chemical unit used to express chemical changes, yet one naturally wonders whether the atom does not consist of something even smaller. The theories and experiments advanced during the past few years,

beginning with a study of the emanations given off by certain minerals containing uranium and thorium, have given scientists much food for thought and investigation.

Some years ago physicists took the view that atomic structure is due to electricity as well as to matter and considered matter as composed of electricity. Since then experiments have resulted in numerous hypotheses some of which are still being investigated and others of which have been either discarded or accepted. The present conception of an atom is that it consists of a minute nucleus of positive electricity surrounded by particles of negative electricity called *electrons*, each having a mass about one seventeen-hundredth ($\frac{1}{1700}$) of that of an atom of hydrogen. The positive charge of electricity tends to draw the *corpuscles*, as electrons are sometimes called, to the center of the sphere, but the repulsion of the electrons from one another tends to drive them apart and away from the center of the sphere, thereby causing them to group themselves in regular order about the nucleus of positive electricity.

It is asserted that each atom contains but a few thousand electrons, though the volume of an atom is capable of holding many times this number. In other words, the electrons are thought to be separate unjoined bodies held in place by charges of electricity.

As the foregoing is still in an experimental stage and as no one hypothesis has been either completely proved or accepted, no further consideration need be given the structure of the atom at this time. Atoms, as the units of chemical changes, still suffice to express the various chemical principles studied in the text.

ELEMENTS AND THEIR COMBINATIONS

23. Elements and Compounds.—There are two kinds of molecules, those that contain similar atoms and those that contain dissimilar ones. Consider, for example, the substance mercuric oxide, each molecule of which contains one atom of mercury and one of oxygen. This substance, when heated, breaks up, or decomposes, into the two substances, mercury

and oxygen. There are no unlike atoms in either of these latter two substances, a molecule of oxygen containing nothing but oxygen atoms and a molecule of mercury nothing but a mercury atom; each is made up of but one kind of atom. So far no one has been able to decompose either mercury or oxygen into simpler substances. Substances that have never been decomposed into simpler ones are called elements, and substances that can be decomposed into simpler substances are called compounds. Elements never contain unlike atoms and compounds always do.

So far as is now known, there are eighty-three substances that have not yet been decomposed into simpler substances. All kinds of matter consist of either these elements or combinations of them. Chlorine, each molecule of which contains 2 atoms of chlorine, is an example of an element. Sodium chloride, commonly called table salt, each molecule of which contains 1 atom of sodium and 1 of chlorine, is an example of a compound.

24. The Atomicities of Molecules.—The number of atoms in the molecules of the different elements is a subject that must be considered at this point, for it has an important bearing on succeeding explanations. Depending upon whether the molecule of an element contains 1, 2, 3, 4, or 6 atoms, it is, respectively, known as monatomic, diatomic, triatomic, tetratomic, or hexatomic. Molecules containing 5 atoms, or pentatomic molecules, are unknown. The atomicities of many of the elements have been determined experimentally, those of others have been found approximately; in a few cases the atomicity is uncertain.

Table I shows the probable atomicity of many of the elements. The atomicities of some of the elements, however, are known to be variable and depend upon the temperature at which the necessary data is obtained. The number of atoms composing the sulphur molecule, for instance, depends upon the temperature. This phenomenon will be more fully discussed when the study of this element is taken up. Because of this variable atomicity, the formula for the sulphur molecule will be written

simply as S in chemical equations representing reactions in which sulphur takes part.

In writing chemical equations involving other elements, the usual atomicities of these elements will be employed

TABLE I

NAMES, ATOMICITIES, AND MOLECULAR FORMULAS OF CHEMICAL ELEMENTS

Atomicity	Name of Element	Molecular Formula	Atomicity	Name of Element	Molecular Formula
Monatomic	Carbon	C	Diatomic	Iodine	I_2
Monatomic	Lithium	Li	Diatomic	Bromine	Br_2
Monatomic	Potassium	K	Diatomic	Chlorine	Cl_2
Monatomic	Sodium	Na	Diatomic	Fluorine	F_2
Monatomic	Barium	Ba	Diatomic	Oxygen	O_2
Monatomic	Strontium	Sr	Diatomic	Hydrogen	H_2
Monatomic	Calcium	Ca	Diatomic	Nitrogen	N_2
Monatomic	Magnesium	Mg	Diatomic	Bismuth	Bi_2
Monatomic	Mercury	Hg	Diatomic	Antimony	Sb_2
Monatomic	Zinc	Zn	Diatomic	Sulphur	S_2
Monatomic	Cadmium	Cd	Diatomic	Tellurium	Te_2
Monatomic	Silver	Ag			
Monatomic	Gold	Au	Triatomic	Ozone	O_3
Monatomic	Lead	Pb			
Monatomic	Argon	Ar	Tetratomic	Phosphorus	P_4
Monatomic	Helium	He	Tetratomic	Arsenic	As_4
Monatomic	Krypton	Kr	Tetratomic	Vanadium	V_4
Monatomic	Neon	Ne			
Monatomic	Xenon	Xe			
Monatomic	Nickel	Ni			
Monatomic	Copper	Cu			
Monatomic	Aluminum	Al			

throughout. Table I shows that practically all the metals are monatomic.

25. Symbols and Formulas.—In indicating the composition of a substance, symbols are used instead of following the somewhat tedious practice of writing in full the names of the different elements involved. The symbols are usually abbreviations consisting of the initial letters of the Latin names

of the elements. As, however, there are over eighty elements and only twenty-six letters in the alphabet, nearly all of the symbols are composed of the initial letter and another distinctive letter selected from the name. Thus, the three elements carbon, chlorine, and copper (cuprum) all have names commencing with the letter *C*; therefore, only carbon has received the letter *C* for its symbol, while *Cl* and *Cu* stand for chlorine and copper, respectively.

26. The application of these symbols for the purpose of showing the elements of a compound may be seen from an example, for which purpose sodium chloride, commonly known as table salt, is selected. Instead of stating that one molecule of sodium chloride contains 1 atom of sodium and 1 atom of chlorine, the expression *NaCl* is used. In this expression the symbol *Na* (Latin, *natrium*) stands for sodium and *Cl* for chlorine. A chemist can ascertain from this expression the exact composition of a molecule of sodium chloride. The compound calcium chloride is represented by its formula, $CaCl_2$, which shows that it contains 1 atom of calcium and 2 atoms of chlorine. Similarly, saltpeter, known chemically as potassium nitrate, contains in each molecule 1 atom of potassium, 1 atom of nitrogen, and 3 atoms of oxygen. The combination may be indicated by the expression KNO_3. The *K* stands for 1 atom of potassium (Latin, *kalium*), the *N* for 1 atom of nitrogen, and O_3 for 3 atoms of oxygen; such a combination of symbols showing the composition of a molecule is called a **formula.**

27. A number placed before a formula is called the **coefficient.** It shows the number of molecules represented. For example, $2KCl$ represents 2 molecules of potassium chloride and $3KNO_3$ stands for 3 molecules of potassium nitrate. The number placed to the right and a little below the symbol of an element is called the **subscript.** It shows the number of atoms of the element contained in 1 molecule. For example, H_2 means that 1 molecule of hydrogen consists of 2 atoms of hydrogen. At this point it must be remembered that molecules are made up of atoms and that, therefore, in the formula of a

compound, we speak of the number of atoms of each element present. Thus, although H_2 represents 1 molecule of hydrogen consisting of 2 atoms, we do not, however, in the formula for water, H_2O, representing 1 molecule of water, think of 1 molecule of hydrogen as being present, but 2 atoms of hydrogen and 1 atom of oxygen. The formula $2K_2SO_4$ represents 2 molecules of potassium sulphate, each molecule of which contains 2 atoms of potassium, 1 atom of sulphur, and 4 atoms of oxygen. It follows that the 2 molecules of potassium sulphate contain, in all, 4 atoms of potassium, 2 atoms of sulphur, and 8 atoms of oxygen. Thus, everything which comes after the coefficient, is multiplied by it. Likewise, the formula $Ca(OH)_2$ represents 1 molecule of calcium hydroxide, which contains 1 atom of calcium, 2 atoms of oyxgen, and 2 atoms of hydrogen, the subscript *2* referring only to the contents of the parenthesis. The formula CaO_2H_2, though also mathematically correct, is not used.

28. The foregoing principles are further illustrated by the following examples: NaI represents 1 molecule of sodium iodide containing 1 atom of sodium and 1 atom of iodine. H_2S represents 1 molecule of hydrogen sulphide containing 2 atoms of hydrogen and 1 atom of sulphur. $2KClO_3$ represents 2 molecules of potassium chlorate, each molecule of which contains 1 atom of potassium, 1 atom of chlorine, and 3 atoms of oxygen; the 2 molecules contain, therefore, 2 atoms of potassium, 2 atoms of chlorine, and 6 atoms of oxygen. $2Ca(NO_3)_2$ represents 2 molecules of calcium nitrate, each molecule of which contains 1 atom of calcium, 2 atoms of nitrogen, and 6 atoms of oxygen; the 2 molecules contain 2 atoms of calcium, 4 atoms of nitrogen, and 12 atoms of oxygen.

After studying the different formulas presented, it may not be quite realized how it is known, for instance, that sodium chloride contains 1 atom of sodium and 1 atom of chlorine. This perplexing problem, however, may be answered by stating that the compound has been analyzed and sodium and chlorine were found in the same proportion as indicated by their atomic weights, which subject will be explained in the succeeding pages.

29. Order of Symbols.—The order in which the symbols of the elements are placed in a formula for a compound depends upon the electrical properties of the element. These properties are designated as electro-positive or electro-negative and for the present purpose it is necessary merely to say that the atom of the element is either positive or negative. It must not be supposed, however, that a sharp line can be drawn between the two classes of atoms.

In electricity it is a well-known fact that positive charges attract negative charges and that negative charges attract positive charges. It is true, too, that positive charges repel positive charges and negative charges repel negative charges. If we keep these facts in mind and apply the principle to positive and negative atoms, it will be seen that compounds are made up of positive and negative atoms. A short list of elements, which will serve as a starting point for formula construction, is given in Table II.

TABLE II

SHORT LIST OF ELEMENTS FOR FORMULA CONSTRUCTION

Positive Elements	Negative Elements
H	*O*
K	*Cl*
Na	*Br*
Ba	*I*
Ca	*S*
Al	*P*
Zn	*N*
Fe	*C*
Sn	*Si*
Pb	

In the table the symbols for the elements have been so arranged that the more strongly positive and negative elements have been placed nearest the top; thus, hydrogen may be regarded as the most positive element of the list and oxygen the most negative, while lead and silicon may be regarded as the least positive and negative, respectively.

30. If now some of the formulas with which we are already familiar are examined it will be seen that most of them are made up of elements contained in Table II, and that in constructing them the positive element is written first. Consider the formulas for sodium chloride, $NaCl$; potassium nitrate,

KNO_3; potassium chloride, KCl; sodium iodide, NaI; hydrogen sulphide, H_2S; potassium chlorate, $KClO_3$; and calcium nitrate, $Ca(NO_3)_2$. In $NaCl$ the positive Na is written first and the negative Cl last; in KNO_3, the positive K is written first, the negative N second, and the still more negative O last; in $KClO_3$, the positive K is written first, the negative Cl second, and the still more negative O, last. In the remaining formulas, KCl, H_2S, NaI, and $Ca(NO_3)_2$, it will be found upon inspection that the statements made concerning the order of symbols holds good. When two symbols are enclosed in parentheses, they represent two elements which act as one and the enclosed portion of the formula is called a **radical.** Thus, (OH) and (NO_3) are known as radicals. This subject will be taken up in detail later on.

31. Forms of Matter.—The divisions of matter so far considered are based on a subdivision by physical and chemical means. There is also a classification based on the freedom with which molecules of matter move about and with their own energy attract one another. The power to attract or hold together one another is called *cohesion* for like molecules, and *adhesion* for unlike molecules.

According to theory, each and every molecule has a vibratory motion. In a solid the molecules are held closely together and kept from getting away from one another by the attractive force between them. Still they are at a considerable distance apart compared with their diameters.

In liquids the distance through which a molecule may move is increased, and the attractive force that binds the molecules together is lessened.

In gases the molecular vibrations have increased to such an extent that the distance between any two molecules has become too great for the attractive force to become effective. The molecules are, therefore, following independent paths and are constantly colliding and rebounding in every direction.

32. Substances pass from one to another of these physical forms under changes of temperature and pressure. If, for example, a piece of ice, a solid, is heated sufficiently, it melts

and forms water, a liquid. The molecules of ice firmly held together by cohesion can retain their original positions without being supported by some external rigid body; that is, a square piece of ice will retain its shape without being supported by some vessel such as a cup or a box. The molecules of water, on the other hand, attract one another to a lesser degree than those of ice and are held together loosely; some external rigid container such as a cup or a glass is needed to hold the liquid in position. Water held in a certain shape by a container will not keep that shape when poured into a container of another shape but will assume the shape of the second container.

If water is heated further, it forms a gas known as *steam*. The molecules of steam tend to follow independent paths and fly off into space, unless held in a closed vessel.

The term vapor is sometimes used to refer to a substance which is at ordinary temperatures either a solid or a liquid, but which has been changed to a gas by the application of heat.

33. Physical Condition of Chemical Elements. Of all the elements, two, mercury and bromine, are ordinarily liquids; eleven of them, oxygen, hydrogen, chlorine, fluorine, nitrogen, argon, helium, krypton, neon, xenon, and niton, are gases; the rest of the elements are solids. Excepting carbon, the solid elements have been changed to liquids by means of heat; so far, carbon has been only slightly softened.

The changing of a solid to a liquid is called fusing or melting; the changing of a liquid to a solid is called freezing or solidifying; the changing of a gas to a liquid is called liquefying; the changing of a solid or a liquid to a gas is called vaporizing. As these terms are used constantly in chemistry they should be thoroughly understood.

34. Mechanical Mixtures and Chemical Compounds.—It is necessary to know when the addition of one substance to another results in a chemical or in a physical change. This distinction can be made clear by considering the mixing of sulphur, *S*, and iron, *Fe* (*ferrum*).

Sulphur is a pale-yellow substance that melts easily when heated and dissolves in carbon disulphide. Iron is a dark-gray

metallic substance that is readily attracted by a magnet and is not soluble in carbon disulphide.

When powdered sulphur and iron filings are rubbed together the product, though differing in appearance from that of either of the constituents, is in reality the two original substances sulphur and iron, the various particles of which are arranged side by side and can be separated from each other by mechanical means. The iron can be removed by passing a magnet over the mixture and sulphur can be freed from iron by treating the mixture with carbon disulphide, a process that dissolves the sulphur and leaves the iron unaffected.

If heat is applied to this mixture of sulphur and iron, a noticeable change takes place, the final result being a black solid, resembling neither iron or sulphur, for it is affected by neither a magnet nor carbon disulphide. It is an entirely new substance known chemically as ferrous sulphide, FeS.

A mixture such as that of sulphur and iron, previous to its being heated, is called a mechanical mixture, which is defined as a collection of substances either elements or compounds that retain their specific properties and can be separated by physical means. A substance such as ferrous sulphide is called a chemical compound, which is defined as a body produced by the chemical reaction between two or more substances and has specific properties different from the specific properties of any of the original substances.

ATOMIC AND MOLECULAR WEIGHTS

35. Atomic Weights.—It would obviously be out of place at this point to discuss all of the methods of obtaining the atomic weights of the elements, but several of the more simple of these will be worked out in detail.

A little reflection will show that the atoms are much too small to have their absolute weights determined, and consequently a standard is selected and the relative weights of the elements as compared to this standard are taken as their atomic weights. As hydrogen is the lightest known element, it was chosen as the standard and its weight called 1. In other words,

the **atomic weight** of an element is the relative weight of an atom of an element compared with that of an atom of hydrogen.

If all the elements formed compounds with hydrogen, the determination of their atomic weights would be a comparatively simple matter, but only a relatively small number of the elements unite directly with hydrogen. In the case of elements like chlorine that unite directly with hydrogen, the combining weight is easily obtained, for if 1 part of hydrogen unites with chlorine, forming 36.19 parts of hydrochloric acid, $36.19-1=35.19$ parts of chlorine must have united with 1 part of hydrogen, and if they united atom for atom, forming HCl, then an atom of chlorine must be 35.19 times as heavy as an atom of hydrogen, or the atomic weight of chlorine is 35.19. Further investigations have shown this to be the correct atomic weight of chlorine.

Likewise, it has been found that there are 15.88 parts by weight of oxygen to every 2 parts of hydrogen in 17.88 parts by weight of water, H_2O. It should be borne in mind that these relative parts by weight are based on the fact that the weight of a hydrogen atom is taken as 1.

It is obvious from the foregoing that an atom of oxygen is 15.88 times as heavy as an atom of hydrogen and that an atom of chlorine is 35.19 times as heavy as an atom of hydrogen.

36. Within recent years the atomic weight system has been altered by making oxygen, instead of hydrogen, the standard of atomic weights. This system is represented by Table III. An examination of water, H_2O, under this system, shows that for every 16 parts by weight of oxygen there are present $2\times1.008=2.016$ parts by weight of hydrogen. The standard, oxygen, is assumed to have an atomic weight of 16 and all other weights are compared with it. As another illustration, calcium oxide, CaO, is found upon analysis to contain calcium and oxygen in the proportion of 40.07 parts of calcium to 16 parts of oxygen; expressed otherwise, an atom of calcium has a relative weight of 40.07, when the atomic weight of oxygen is taken as 16. Values such as 1.008, for hydrogen, and 40.07, for calcium, are called the atomic weights of these elements, when

TABLE III

INTERNATIONAL ATOMIC WEIGHTS, 1925

Name	Symbol	Atomic Weight	Name	Symbol	Atomic Weight
Aluminum	*Al*	26.97	Mercury (Hydrargyrum)	*Hg*	200.61
Antimony (Stibium)	*Sb*	121.77	Molybdenum	*Mo*	96.0
Argon	*A*	39.91	Neodymium	*Nd*	144.27
Arsenic	*As*	74.96	Neon	*Ne*	20.2
Barium	*Ba*	137.37	Nickel	*Ni*	58.69
Bismuth	*Bi*	209.0	Nitrogen	*N*	14.008
Boron	*B*	10.82	Osmium	*Os*	190.8
Bromine	*Br*	79.916	Oxygen	*O*	16.0
Cadmium	*Cd*	112.41	Palladium	*Pd*	106.7
Cæsium	*Cs*	132.81	Phosphorus	*P*	31.027
Calcium	*Ca*	40.07	Platinum	*Pt*	195.23
Carbon	*C*	12.0	Potassium (Kalium)	*K*	39.096
Cerium	*Ce*	140.25	Praseodymium	*Pr*	140.92
Chlorine	*Cl*	35.457	Radium	*Ra*	225.95
Chromium	*Cr*	52.01	Radon (Niton)	*Rn*	222
Cobalt	*Co*	58.94	Rhodium	*Rh*	102.91
Columbium	*Cb*	93.1	Rubidium	*Rb*	85.44
Copper (Cuprum)	*Cu*	63.57	Ruthenium	*Ru*	101.7
Dysprosium	*Dy*	162.52	Samarium	*Sa*	150.43
Erbium	*Er*	167.7	Scandium	*Sc*	45.1
Europium	*Eu*	152.0	Selenium	*Se*	79.2
Fluorine	*F*	19.0	Silicon	*Si*	28.06
Gadolinium	*Gd*	157.26	Silver (Argentum)	*Ag*	107.88
Gallium	*Ga*	69.72	Sodium (Natrium)	*Na*	22.997
Germanium	*Ge*	72.6	Strontium	*Sr*	87.63
Glucinum (Beryllium)	*Gl*	9.02	Sulphur	*S*	32.064
Gold (Aurum)	*Au*	197.2	Tantalum	*Ta*	181.5
Hafnium	*Hf*	180.8	Tellurium	*Te*	127.5
Helium	*He*	4.0	Terbium	*Tb*	159.2
Holmium	*Ho*	163.4	Thallium	*Tl*	204.39
Hydrogen	*H*	1.008	Thorium	*Th*	232.15
Indium	*In*	114.8	Thulium	*Tm*	169.4
Iodine	*I*	126.932	Tin (Stannum)	*Sn*	118.7
Iridium	*Ir*	193.1	Titanium	*Ti*	48.1
Iron (Ferrum)	*Fe*	55.84	Tungsten	*W*	184.0
Krypton	*Kr*	82.9	Uranium	*U*	238.17
Lanthanum	*La*	138.9	Vanadium	*V*	50.96
Lead (Plumbum)	*Pb*	207.2	Xenon	*Xe*	130.2
Lithium	*Li*	6.94	Ytterbium (Neoytterbium)	*Yb*	173.6
Lutecium	*Lu*	175.0	Yttrium	*Yt*	88.9
Magnesium	*Mg*	24.32	Zinc	*Zn*	65.38
Manganese	*Mn*	54.93	Zirconium	*Zr*	91.0

oxygen is taken as the standard with a value of 16. Therefore, according to modern views, the **atomic weight** of an element is the relative weight of an atom of that element compared with the weight of an atom of oxygen which has a value of 16.

37. The plan followed in determining the atomic weight of zinc illustrates clearly the methods actually used in determining the atomic weights of the solid elements.

1. Hydrochloric or sulphuric acid is allowed to act on zinc, liberating hydrogen, and if a known weight of zinc is used, the weight of zinc necessary to liberate 1 gram of hydrogen is easily calculated. This number is the equivalent of zinc, and since 1 atom of zinc replaces 1 atom of hydrogen, then the ratio of the atomic weight of zinc to the atomic weight of hydrogen will be the same as the weight of zinc to the weight of hydrogen. According to this, the equivalent of zinc is 32.685, and thus far its atomic weight.

2. When zinc and hydrochloric acid react together zinc chloride is formed. On analysis the proportion of zinc to chlorine is found to be about 32.685 to 35.46. Now, assuming the elements to combine atom for atom and that the atomic weight of chlorine is 35.46, the atomic weight of zinc is 32.685.

3. Zinc oxide is formed when zinc is burned in air, and when this compound is analyzed the proportion of zinc to oxygen is 65.37 to 16. Hence, if the elements combine atom for atom the atomic weight of zinc is 65.37.

According to these three determinations zinc has the atomic weight of 32.685 or 65.37. The assumption has been that the elements unite atom for atom, but this assumption must be incorrect, because zinc like all other metals can have but one atomic weight. If the atomic weight of zinc is taken as 32.685, then zinc oxide must be composed of 1 atom of oxygen and 2 atoms of zinc; whereas, if the figure 65.37 is used zinc chloride must consist of 1 atom of zinc and 2 atoms of chlorine, and 2 atoms of hydrogen must have been replaced by 1 atom of zinc.

Determined by the vapor-density method, which is described in *Organic Chemistry*, the weight of a molecule of zinc chloride was found to be 133. Now, if zinc chloride consists of 2 atoms

of chlorine and 1 atom of zinc, and the atomic weight 65.37 is used, its molecular weight is 136.29. Hence, the assumption regarding the number of atoms in zinc chloride is probably correct. However, there is no absolute certainty whether the zinc in zinc chloride is 1 atom weighing 65.37 or whether it is 2 atoms each weighing 32.685. The approximate atomic weight determined by applying the law of specific heats is found to be (6.25 divided by 0.094) 66.4. Hence, this shows clearly that the atomic weight of zinc must be 65.37.

Atomic weights can be determined also by analysis when the proportion in which the atoms combine to form a molecule of the compound analyzed is known. Thus, 66.434 grams of silver chloride are formed by burning 50 grams of silver in chlorine. Now, it is known that 1 atom of silver unites with 1 atom of chlorine to form silver chloride, and since the atomic weight of chlorine is 35.46, the calculated atomic weight of silver is obtained thus:

$$66.434 - 50 = 16.434$$

which is the weight of the chlorine used. Then,

$$50 : 16.434 = x : 35.46, \text{ and } x = 107.88$$

the atomic weight of silver.

The approximate atomic weight of solids can be checked by the law of specific heats announced by Dulong and Petit. This is that the product of the specific heat and atomic weight of the solid elements is a constant quantity.

By **specific heat** is meant the quantity of heat necessary to raise the temperature of the substance 1 degree compared with the quantity of heat necessary to raise the temperature of the same weight of water 1 degree. The constant quantity obtained by multiplying the specific heat by the atomic weight is approximately 6.25, as will be found by averaging the products shown in Table IV.

38. This use of the law is illustrated as follows: The specific heat of silver is .0570, and this divided into 6.25 gives the approximate atomic weight of silver as 109. This agrees very closely with 107.88, the true atomic weight. This law has been of great assistance in determining the atomic weights

of several elements, as, for example, that of uranium, which was finally accepted as 238.2 instead of 119.25. Both of these values agree with analyses, but the former conforms to the law of specific heat.

39. Molecular Weights.—If one knows the number of atoms and the atomic weights of the elements in a molecule, he can easily find the molecular weight of the compound. In every case the molecular weight of a molecule is the sum of its atomic weights. The molecular weight of any compound is then equal to the sum of the atomic weights as represented by the number of atoms in the molecule. Thus, a molecule of water contains 2.016 parts by weight of hydrogen and 16 parts of oxygen.

TABLE IV

SPECIFIC HEAT CONSTANT

Element	Specific Heat	Atomic Weight	Product
Bismuth	.0308	208.0	6.40
Cobalt	.1067	58.97	6.29
Copper	.0968	63.57	6.15
Iron	.1138	55.84	6.35
Nickel	.1092	58.68	6.41
Sulphur	.1844	32.07	5.91

Its molecular weight is the sum of the weights of all the atoms present in the molecule, in this case 2.016+16, or 18.016.

One should learn to apply the atomic and molecular weights to calculations, for they are used in every phase of chemistry and are indispensable to the chemist in industrial work. The application of Table III is shown by means of the following examples:

EXAMPLE 1.—Find the molecular weight of KCl, potassium chloride.

SOLUTION.—The formula shows that 1 molecule of potassium chloride contains 1 atom of each element. Hence, the weights given in Table III may be applied directly. Or,

Atomic weight of chlorine $=35.46$
Atomic weight of potassium $=39.10$

Molecular weight of potassium chloride $=74.56$. Ans.

EXAMPLE 2.—Find the molecular weight of Na_2O, sodium oxide.

SOLUTION.—According to the formula there are 2 atoms of sodium, Na. The weight given in Table III must therefore be multiplied by 2. Or,

2×atomic weight of sodium	= 46.00
Atomic weight of oxygen	= 16.00
Molecular weight of Na_2O	= 62.00. Ans.

EXAMPLE 3.—Find the molecular weight of Na_2SO_4, sodium sulphate.

SOLUTION.—The formula shows that there are 2 atoms of Na and 4 atoms of O; hence, the atomic weights of these elements must be multiplied by 2 and 4, respectively. Or,

2×atomic weight of sodium	= 46.00
Atomic weight of sulphur	= 32.06
4×atomic weight of oxygen	= 64.00
Molecular weight of Na_2SO_4	= 142.06 Ans.

EXAMPLE 4.—Find the molecular weight of $Ba(OH)_2$, barium hydroxide.

SOLUTION.—In Art. 27 it was stated that the subscript 2 refers to the contents of the parenthesis; that is, O and H. There must, therefore, be 2 atoms of each. Or,

Atomic weight of barium	= 137.370
2×atomic weight of oxygen	= 32.000
2×atomic weight of hydrogen	= 2.016
Molecular weight of $Ba(OH)_2$	= 171.386. Ans.

EXAMPLE 5.—Find the molecular weight of $CaOCl_2$, chloride of lime.

SOLUTION.—In this example there is 1 atom of each element, except chlorine, of which there are 2. Hence,

Atomic weight of calcium	= 40.07
Atomic weight of oxygen	= 16.00
2×atomic weight of chlorine	= 70.92
Molecular weight of $CaOCl_2$	= 126.99. Ans.

NOTE.—The following Examples for Practice should be solved in the manner shown in the preceding examples, so as to acquire facility in calculations of this kind.

EXAMPLES FOR PRACTICE

Find the molecular weight of:

1. $CaCO_3$, calcium carbonate. Ans. 100.075
2. $PbCrO_4$, lead chromate. Ans. 323.20
3. $K_3Fe(CN)_6$, potassium ferricyanide. Ans. 329.218
4. $Mg(NH_4)_2(SO_4)_2$, magnesium ammonium sulphate. Ans. 252.52
5. $K_2Cr_2O_7$, potassium bichromate. Ans. 294.2

CHEMICAL AFFINITY AND VALENCE

40. Attraction of Atoms.—On noting the many varied chemical changes in nature, one is apt to wonder whether there is not some force or power that causes them. It is well, therefore, to consider this subject before proceeding further with the study of chemical laws and definitions. When atoms of elements unite to form molecules of new compounds, they do so in such a manner that the forces of attraction of each atom for the other is satisfied. For instance, when the elements sodium and chlorine are brought together, the compound sodium chloride, $NaCl$, consisting of 1 atom of sodium and 1 atom of chlorine, is formed. The chemical affinity of each atom in this compound is said to be *satisfied* because it can be shown that the Cl will not unite with any additional atoms of Na, nor will the Na unite with additional atoms of Cl. In a similar manner when calcium and chlorine are brought together, the compound calcium chloride, $CaCl_2$, is formed. Here 2 atoms of Cl are required to satisfy the chemical attraction or affinity which calcium has for chlorine.

41. Valence.—The element hydrogen is frequently used in the study of chemistry as a standard of comparison. Until recently it was used as a standard for the atomic weight system, the value assigned to it being 1. Hydrogen is also used as a standard of density for gases and, in the case of valence, hydrogen also serves as the standard and is given a value, or a valence, of 1, and the valences of all other elements are compared with it.

Valence should not be confused with chemical affinity, for each has its own distinctive chemical significance. Valence refers to the number of atoms of one element that can unite with an atom of another element, while chemical affinity treats of the relative force of attraction possessed by elements. An illustration will probably make this distinction clear. The elements chlorine and sodium have been found by experiment to have a greater chemical affinity for each other than have chlorine and calcium, yet 1 atom of calcium can unite with

twice as many chlorine atoms as 1 atom of sodium, because calcium has a valence twice that of sodium. If all three elements are present, chlorine and sodium will unite much more readily than will chlorine and calcium, because the chemical affinity between chlorine and sodium is greater than that between chlorine and calcium. It is obvious, therefore, that chemical affinity and valence have entirely different meanings.

42. When studying the subjects of symbols and formulas and molecular weights, chemical formulas were used for illustrative purposes and it was noticed that certain elements such as hydrogen, H, and chlorine, Cl, combined with each other, atom for atom, and formed the compound hydrochloric acid, HCl. Therefore, since it is true that when atoms of different elements combine, the chemical affinity and the valence of each must be satisfied, and again since the valence of H is taken as 1, that of chlorine must also be 1. We have also mentioned the compounds sodium chloride, $NaCl$, and calcium chloride, $CaCl_2$, and, applying the reasoning used in establishing the valence of chlorine in the compound HCl, we arrive at the conclusion that since chlorine has a valence of 1 in HCl, it may also have a valence of 1 in $NaCl$. This is actually the case, and the valence of Na must also be 1. Taking up the case of calcium in calcium chloride, we note that there are 2 atoms of chlorine and since each atom has a valence of 1, the total valence must be 2; therefore, calcium has a valence of 2. In other words, calcium has a valence equivalent to 2 hydrogen atoms.

43. Valence is correctly defined as the combining capacity of 1 atom of an element and is indicated by the number of hydrogen atoms with which an atom of the element in question will unite, or by the number of hydrogen atoms or its equivalent, an atom of the element will replace.

The following illustration will make the definition more clear: Take the compound water, the formula for which is H_2O. The valence of hydrogen is 1 and since there are 2 atoms of hydrogen in this formula, there is also a total of 2 valences for hydrogen, and since the valences of each element must be satisfied, the

valence of oxygen must also be 2, and it is worth noting here that in all its compounds oxygen has always been found to have a valence of 2. As another example, take the compound sodium oxide, the formula for which is Na_2O. We have already established the valence of sodium in the compound sodium chloride, $NaCl$, as being 1 and that of oxygen in H_2O as being 2. Therefore, when sodium and oxygen are brought together and react, a compound of sodium and oxygen is formed and, since oxygen has a valence of 2, 2 atoms of sodium with a total valence of 2 must be present in the compound.

44. Upon inspecting Table V, the student will find that some of the elements have more than one valence. In other words, it will be found that the valence of some of the elements listed depends upon the element with which they combine. A variable valence should not necessarily be confusing, however, if the valences of a few of the common elements are remembered. Thus, hydrogen, H, always has a valence of 1, oxygen, O, a valence of 2, and sodium and potassium 1.

Among the common elements which have a variable valence are chlorine, Cl, and nitrogen, N. The particular valence of either of these elements in any of their compounds can, however, easily be worked out. Thus some of the commoner compounds which nitrogen forms are nitrous oxide, N_2O; nitric oxide, NO; nitrogen dioxide, NO_2; nitrogen trioxide, N_2O_3; and nitrogen pentoxide, N_2O_5. In N_2O nitrogen has a valence of 1, since oxygen always has a valence of 2 and $2N$ with a total valence of 2 are required to satisfy the valence of oxygen. In NO the valence of N must be 2, since 1 atom of it has combined with 1 atom of oxygen, which has a valence of 2. In NO_2 the valence of N is 4 since 2 atoms of oxygen have a total valence of 4. In N_2O_3 there are 6 valences for 3 oxygen atoms, and since there are only $2N$, the valence of each must be 3. In N_2O_5 there are a total of 10 valences for oxygen, therefore each N must have a valence of 5.

Nitrogen is also a constituent of nitric acid, the formula for which is HNO_3. Here there are 6 valences for oxygen and 1 for hydrogen, leaving 5 for nitrogen.

TABLE V

USUAL VALENCE OF ELEMENTS

Name of Element	Symbol	Valence	Name of Element	Symbol	Valence
Aluminum........	*Al*	3	Nickel..........	*Ni*	2, 3
Antimony (Stib-			Nitrogen........	*N*	1,2,3,4,5
ium)...........	*Sb*	3, 5	Osmium.........	*Os*	2 to 8
Arsenic..........	*As*	3, 5	Oxygen.........	*O*	2
Barium..........	*Ba*	2	Palladium.......	*Pd*	2, 4
Bismuth.........	*Bi*	3, 5	Phosphorus......	*P*	3, 5
Boron............	*B*	3	Platinum........	*Pt*	2, 4
Bromine.........	*Br*	1, 3, 5, 7	Potassium		
Cadmium........	*Cd*	2	(Kalium)	*K*	1
Cæsium	*Cs*	1	Praseodymium ..	*Pr*	3
Calcium..........	*Ca*	2	Rhodium........	*Rh*	2, 3, 4
Carbon..........	*C*	4	Rubidium.......	*Rb*	1
Cerium..........	*Ce*	3, 4	Ruthenium......	*Ru*	2 to 8
Chlorine.........	*Cl*	1, 3, 5, 7	Samarium.......	*Sa*	3
Chromium........	*Cr*	2, 3, 6	Scandium.......	*Sc*	3
Cobalt...........	*Co*	2, 3	Selenium........	*Se*	2, 4, 6
Copper (Cuprum).	*Cu*	1, 2	Silicon..........	*Si*	4
Erbium..........	*Er*	3	Silver(Argentum)	*Ag*	1
Fluorine..........	*F*	1, 3	Sodium		
Gallium..........	*Ga*	3	(Natrium)	*Na*	1
Germanium	*Ge*	2, 4	Strontium.......	*Sr*	2
Glucinum (Beryl-			Sulphur.........	*S*	2, 4, 6
lium)..........	*Gl*	2	Tantalum.......	*Ta*	5
Gold (Aurum)....	*Au*	1, 3	Tellurium.......	*Te*	2, 4, 6
Hydrogen........	*H*	1	Terbium........	*Tb*	3
Indium..........	*In*	3	Thallium........	*Tl*	1, 3
Iodine...........	*I*	1, 3, 5, 7	Thorium........	*Th*	4
Iridium..........	*Ir*	3, 4	Tin (Stannum) ..	*Sn*	2, 4
Iron (Ferrum)....	*Fe*	2, 3, 6	Titanium........	*Ti*	3, 4
Lanthanum.......	*La*	3	Tungsten........	*W*	2 to 6
Lead (Plumbum) .	*Pb*	2, 4	Uranium........	*U*	4, 6
Lithium..........	*Li*	1	Vanadium.......	*V*	2 to 5
Magnesium.......	*Mg*	2	Ytterbium		
Manganese.......	*Mn*	2,3,4,6,7	(Neoytterbium)	*Yb*	3
Mercury			Yttrium.........	*Yt*	3
(Hydrargyrum).	*Hg*	1, 2	Zinc............	*Zn*	2
Molybdenum.....	*Mo*	2, 3, 4, 6	Zirconium.......	*Zr*	4
Neodymium......	*Nd*	3			

The compounds of chlorine in which the valence varies are also numerous, but the valence can be worked out in exactly the same manner as for nitrogen. Thus, in the compound potassium chlorate, $KClO_3$, there are 6 valences for 3 oxygen atoms, 1 valence for potassium, leaving 5 for chlorine. In the compound sodium perchlorate, $NaClO_4$, there are 8 valences for oxygen, 1 for sodium, leaving 7 for chlorine.

TABLE VI

DIFFERENT VALENCES AND THEIR DESIGNATIONS

Valence	Element is said to be	Element is called a
1	Monovalent, or univalent	Monad
2	Divalent, or bivalent	Dyad
3	Trivalent, or tervalent	Triad
4	Tetravalent, or quadrivalent	Tetrad
5	Pentavalent, or quinquivalent	Pentad
6	Hexavalent, or sexivalent	Hexad
7	Heptavalent, or septavalent	Heptad
8	Octavalent	Octad

45. Designation of Valence.—The subject of variable valence has been sufficiently explained to make it clearly understood, and it is now merely necessary to show by means of Table VI how the valence of an element is designated.

CHEMICAL EQUATIONS AND THEIR INTERPRETATION

46. When the subject of chemical and physical changes was discussed, it was stated that when a substance was changed to an altogether different substance having a different chemical composition than the original substance, a chemical change had taken place. We can now go a few steps farther and give this so-called chemical change the name by which it is always

designated. In other words, when the chemical composition of a substance has been changed a *chemical reaction* must have taken place.

47. Up to this point a single substance only has been dealt with, but chemical reactions are not limited to single substances. In fact, the majority of reactions occur between two or more substances. Thus, when two substances are heated together, and if they react, or if a chemical reaction occurs, the identity of each substance is lost and a new product, called the product of the reaction, is formed. For example, if a quantity of iron filings were mixed with powdered sulphur or flowers of sulphur, and the mixture strongly heated, a compound of iron and sulphur would be formed. This compound, known as ferrous sulphide, would have properties differing greatly from those of the original iron or sulphur.

It has already been shown that elements and compounds are represented by symbols and formulas, and in the writing of chemical equations these are employed.

48. In the case of the reaction between iron and sulphur by which ferrous sulphide is formed, the statement might merely be made that when iron and sulphur are heated together, the product is ferrous sulphide, but by representing this reaction by means of the equation,

$$Fe + S + \text{heat} = FeS$$

several advantages are gained. At a glance this equation shows to a chemist, that when iron and sulphur are heated together ferrous sulphide is formed. Ordinarily the word *heat*, would not be written into the equation, it being assumed that the reader knows that the reaction would not take place without the aid of heat.

49. In connection with equation writing, the question is often asked concerning the identity of the products of a reaction. This question can be answered only by saying that in the beginning of the science of chemistry it was not known what was formed when different substances reacted. Therefore, it

was necessary to devise methods of analysis so that these new products might be identified. In this way the products formed, as the result of most chemical reactions, are known, and if they are not known, their identity and composition must be established by methods peculiar to analytical chemistry.

50. Upon further examination of the foregoing equation it will be noted that the number of iron and sulphur atoms on each side of the equality sign is the same. In other words, the equation may be said to balance. This is an important point to be remembered, since chemical equations cannot be correct unless they balance.

51. Facts Concerning Chemical Equations.—Before going deeper into the subject of equation writing, it will be well to introduce a few rules for the application and guidance of the beginner in chemistry.

1. A true chemical equation is a statement of a fact, therefore *if an equation is written for a reaction that cannot take place —the equation is obviously incorrect.* In other words, chemical equations are correct only when the changes they represent actually take place.

2. *The number of atoms of any element on each side of the equality sign of an equation must be the same.*

3. *The atomicities of the elements must be observed when the symbols representing the elements are placed in an equation.*

4. *The products of most reactions have been analyzed and must be remembered.*

Apply the four points just given to the only equation which we have thus far studied, namely: $Fe+S=FeS$.

In the first place, it is known that the reaction takes place, so the equation may be written to represent it; with respect to the second point, the number of atoms of each element on one side of the equality sign is the same; and, in the third place, the symbols for iron and sulphur are written in accordance with what we know concerning the atomicity of each. It is also known that FeS is formed because the product has been analyzed. It is seen, therefore, that the equation is correctly written.

52. Balancing Simple Equations.—In this discussion, the manner in which simple chemical equations may be balanced is shown. The equations chosen for the purpose of illustration conform to two of the statements previously made, that is, they represent reactions which actually take place and the products of each reaction are known.

The first equation to be considered is that representing the reaction which takes place between sodium chloride, $NaCl$, and sulphuric acid, H_2SO_4. The products of this reaction are sodium sulphate, Na_2SO_4, and hydrochloric acid, HCl. The incomplete, or *skeleton*, equation may then be written:

$$NaCl+H_2SO_4=Na_2SO_4+HCl$$

Upon inspection it will readily be seen that this equation does not balance for the following reasons: On the left-hand side of the equation there is only 1 sodium (Na) atom while on the right-hand side there are 2 sodium (Na) atoms. Again, on the left there are 2 hydrogen (H) atoms and on the right there is only 1 hydrogen (H) atom. To complete this equation then, it is necessary to cause the Na atoms to balance by writing $2NaCl$ on the left, thus:

$$2NaCl+H_2SO_4=Na_2SO_4+HCl$$

As the result of this, however, there are now 2 chlorine (Cl) atoms on the left and only 1 chlorine (Cl) atom on the right, and it is necessary to balance both the H and the Cl atoms. This is easily accomplished by writing $2HCl$ on the right-hand side of the equation, thus:

$$2NaCl+H_2SO_4=Na_2SO_4+2HCl$$

Upon inspecting the equation now, it will be found that the number of atoms of each element on each side of the equality sign is the same. In other words, the equation is balanced.

53. As a second example, consider the formation of hydrogen and ferrous chloride, $FeCl_2$, when hydrochloric acid is brought in contact with iron, Fe. The skeleton equation may be written

$$Fe+HCl=FeCl_2+H_2$$

In this case there are 2 chlorine atoms and 2 hydrogen atoms on the right and only 1 of each on the left, but to cause the

equation to balance it is necessary to write $2HCl$ on the left-hand side, thus:

$$Fe+2HCl=FeCl_2+H_2$$

in which all of the atoms balance.

54. Use of Valence in Writing Chemical Equations. If the principles of valence have been thoroughly studied, their application to the writing of correct chemical equations should present little or no difficulty. It is not always necessary that the principles of valence be considered in balancing equations. Some types of equations which will be taken up later cannot be balanced without taking the valence of the different elements into consideration. Therefore, the application of valence to the writing of simple equations will be illustrated at this point in order to render the work of balancing more complicated equations less difficult. To begin with, consider the reaction which takes place when iron rusts. To make the work as simple as possible, the rusting of iron may be said to be due to the action of atmospheric oxygen on the iron, the product of the reaction being ferric oxide, Fe_2O_3. The skeleton equation for this reaction is written

$$Fe+O=Fe_2O_3$$

Oxygen, however, is diatomic and is written O_2, so the equation becomes

$$Fe+O_2=Fe_2O_3$$

This equation can be balanced by the methods given in preceding examples, but not readily, and the processes previously used applied to this equation resolve themselves into hit-or-miss methods, which, as far as practical results are concerned, are useless.

For example, an attempt might be made to balance the equation by first making the Fe atoms equal, thus:

$$2Fe+O_2=Fe_2O_3$$

It is not as simple a matter, however, to make the oxygen atoms balance. In fact, it can only be done by using a fractional coefficient, $1\frac{1}{2}$, before the O_2, which would give 3 oxygen atoms on the left. Fractional coefficients are not used in equation writing, so, having written the equation

$$2Fe+1\tfrac{1}{2}O_2=Fe_2O_3$$

it is necessary that it be multiplied throughout by 2 in order to get rid of the fractional coefficient. When this has been done the equation has been correctly balanced and is written

$$4Fe+3O_2=2Fe_2O_3$$

Using the valences of the elements, when an equation cannot be readily balanced by other methods, the process becomes a short and simple one. Thus, in the equation

$$Fe+O_2=Fe_2O_3$$

Fe on the left has a valence of zero, since it is not in combination, while on the right, Fe has a valence of 3; or there is a total difference of 3 in valence. This difference must have been due to the action of oxygen, so the 3 is placed before the O_2 and the equation at once becomes

$$Fe+3O_2=Fe_2O_3$$

Now, the preceding methods may be used and to have 6 oxygen atoms on the right, Fe_2O_3 must be multiplied by 2, which gives 4 Fe atoms on the right, making necessary that $4Fe$ also appears on the left, thus:

$$4Fe+3O_2=2Fe_2O_3$$

55. In connection with the subject of equation writing, a question frequently asked, by those beginning the study of the subject of chemistry, is, "How can I tell what the products of a certain reaction will be?" As an answer to this question, it may be stated that where one's chemical experience is very limited, as in the case of a beginner, the memory must be depended upon largely or reference made to the text to determine the course of a certain reaction. However, as a student of chemistry gradually becomes familiar with all types of chemical reactions, a certain similarity will be noticed between them. For instance, it will be seen that when acids act on carbonates the usual products are in part carbon dioxide and water. Thus, $Na_2CO_3+2HCl=2NaCl+CO_2+H_2O$. The temperature at which a reaction takes place, whether in a hot or cold solution, sometimes determines whether certain products or others will be formed; and again, quantities of materials,

strengths of acids and solutions, and other factors determine what will happen when compounds react.

56. The ability to predict what will be formed as the result of a simple chemical reaction depends upon one's knowledge of the effect of the above factors and others which will be taken up later. This knowledge can be gained only by a thorough study of all of the reactions represented by equations given in the text. If this procedure is followed the beginners will soon find that they have learned all of the principal reactions and eventually all of those which they meet in subsequent work will in most respects be similar to those which they have already studied.

57. Interpretation of Chemical Equations.—A further study of chemical equations reveals another fact by which their accuracy can be judged. The equation representing the fact that 2 molecules of hydrochloric acid can be decomposed into 1 molecule of hydrogen and one of chlorine, is as follows:

$$2HCl = H_2 + Cl_2$$

Each molecule of hydrochloric acid consists of 1 atom of hydrogen and 1 of chlorine; 2 molecules contain 2 atoms of hydrogen and 2 of chlorine. Likewise, 1 molecule of hydrogen contains, according to Table I, 2 atoms of hydrogen, and 1 molecule of chlorine contains 2 atoms of chlorine. There are, therefore, 4 atoms on each side of the equation, consisting of 2 atoms of chlorine and 2 atoms of hydrogen.

If now, the atomic weight of each element is placed over its symbol in the equation and the proper multiplications and additions are made, it will be found that the sum of the atomic weights, or the molecular weights on each side of the equation, is equal. Thus, the molecular weight of hydrochloric acid, as found by adding the atomic weights of hydrogen and chlorine. is 36.468; $2HCl$ has a relative weight of $2 \times 36.468 = 72.936$. Likewise, 1 molecule of chlorine and 1 molecule of hydrogen have the respective molecular weights 70.92 and 2.016; the sum is 72.936. It is apparent that the sum of the atomic weights on each side of this chemical equation is the same, as both are equal to 72.936.

Consider the reaction which takes place between the compound barium chloride, $BaCl_2$, and sulphuric acid. The completed equation is written

$$BaCl_2+H_2SO_4=BaSO_4+2HCl$$

The sum of the weights on each side of the equation can be shown to be the same as follows:

The molecular weight of barium chloride is	208.290
The molecular weight of sulphuric acid is	98.076
Total	306.366
The molecular weight of barium sulphate is	233.430
Twice the molecular weight of hydrochloric acid is	72.936
Total	306.366

When the molecular weights of the compounds involved in a reaction are written over the formulas representing the compounds, an interesting fact is illustrated. Thus, in the reaction between barium chloride and sulphuric acid, the equation written

$$\frac{208.29}{BaCl_2}+\frac{98.076}{H_2SO_4}=\frac{233.43}{BaSO_4}+\frac{72.936}{2HCl}$$

shows that when 208.29 parts by weight of barium chloride combine with 98.076 parts by weight of sulphuric acid, they form 233.43 parts by weight of barium sulphate and 72.936 parts by weight of hydrochloric acid. The parts by weight may be expressed in terms of any unit of weight, such as ounces, pounds, or in the units of the metric system.

58. Use of Relative Weights.—The preceding explanations show that equations enable the chemist to determine a number of facts from the relative atomic weights. The application of relative weights in chemical equations is sufficiently important to be touched on briefly before proceeding to another subject.

The relative weights represented in a chemical equation, called combining weights, are used to calculate the weights of substances needed to produce a desired compound. For example, calcium carbonate has been found by experiment

to break up when heated, into calcium oxide and carbon dioxide in this way:

$$CaCO_3 = CaO + CO_2$$

Combining weights:

$$100.075 = 56.07 + 44.005$$

This equation is correctly written, for it represents a chemical change that actually takes place and it has the same number of atoms of each element and the same sum of combining weights on each side. Furthermore, the combining weights of the substances, calculated from Table III, show that every 100.075 parts by weight of calcium carbonate break up, when heated, into 56.07 parts by weight of calcium oxide and 44.005 parts by weight of carbon dioxide.

A chemist in his work may be asked to calculate the number of tons of calcium carbonate needed to produce 44.005 tons of carbon dioxide and also the number of tons of calcium oxide produced. Relative weights form the basis for just such calculations as this one and are constantly applied in chemical work. It has already been shown that 100.075 parts by weight will produce 44.005 parts by weight of carbon dioxide and 56.07 parts by weight of calcium oxide. Hence, 100.075 tons of calcium carbonate are needed to produce 44.005 tons of carbon dioxide, while 56.07 tons of calcium oxide are left. In like manner, if the weight of either calcium carbonate or calcium oxide is given, one can calculate the weights of the other substances formed or needed.

CONSERVATION AND TRANSFORMATION OF MATTER

59. Indestructibility of Matter.—A study of chemical changes shows that the sum of the weights of the substances used is equal to the sum of the weights of the products formed. Consider again, for example, the change that takes place when barium chloride is acted on by sulphuric acid. Or,

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$$

From the atomic weights of the elements present, it is apparent, as previously shown, that 208.29 parts by weight of barium chloride and 98.076 parts by weight of sulphuric acid produce 233.43 parts by weight of barium sulphate, and 72.936 parts by weight of hydrochloric acid; that is, 306.366 parts by weight of the substances used form 306.366 parts by weight of products. In other words, the sum of the weights of materials used is equal to the sum of the weights of the products formed.

The fact that neither more nor less by weight of products is formed than is used, is true of all chemical changes and leads to an important chemical law, which may be expressed in this way: *Whenever a change takes place in the composition of substances, the weight of matter after the change is the same as the weight before the change.*

60. Conservation of Energy.—Closely allied to the law regarding the indestructibility of matter is the law relating to the conservation of energy. Heat, light, and electricity all have capacities for doing work; each of these agencies can bring about physical and chemical changes. These influences are forms of **energy**, which is the capacity of a body for doing work. Unlike matter, energy neither has weight nor occupies space.

In all chemical changes energy is given off or absorbed. If, for instance, calcium oxide, commonly called quicklime, is mixed with water, considerable energy in the form of heat is given off and slaked lime is produced. Thus,

$$CaO + H_2O = Ca(OH)_2$$

Similarly, energy in the form of heat must be added to change calcium carbonate into calcium oxide and carbon dioxide.

The various forms of energy can be converted into one another. Suppose, for example, that the heat under a boiler in an electric plant is used to generate steam which in turn causes an engine to produce motion; the motion can be used to run a dynamo and produce electricity; if the current of electricity is passed through an incandescent lamp, light and heat are evolved. It is seen that the form of energy, heat,

passes to other forms, such as motion, electricity, and light. If it were possible to produce these transformations in some form of apparatus from which no form of energy could escape, the amount of energy at the beginning of the transformation would be found to be the same as that at the finish. The fact that neither a creation nor a destruction of energy has ever been observed has resulted in the law regarding the conservation of energy, expressed as follows: Energy cannot be created or destroyed.

61. Chemical Energy.—One naturally wonders where the coal gets its heat since energy cannot be created. The coal burns, that is, combines with oxygen to form carbon dioxide, thus,

$$C + O_2 = CO_2$$

A considerable amount of energy in the form of light and heat is liberated during this change. It is, therefore, apparent that there was some kind of energy stored up in the coal and that it was liberated when the coal reacted with oxygen to form carbon dioxide. Like all other forms of energy, that one contained in the coal, called chemical energy, has a capacity for doing work. Chemical energy is stored up in many substances other than coal. Thus, the heat liberated when calcium oxide is mixed with water is chemical energy contained in the former.

It is apparent from the foregoing that chemical changes are always accompanied by some kind of an energy transformation; chemical energy may be changed to some other form, or another form may be converted into chemical energy.

62. Exothermic and Endothermic Reactions. When substances react to form new compounds, heat is either given off or it is absorbed. This absorption or evolution of heat may not be apparent, but nevertheless it may be measured by the use of suitable apparatus.

Those reactions in which heat is given off are described as exothermic. Examples are the formation of *NaOH* when sodium and water react, or when hydrogen and chlorine react to form hydrochloric acid. An endothermic reaction is just the reverse of the above; that is, in this type, heat is absorbed.

The formation of carbon bisulphide from carbon and sulphur, or the formation of chlorine and hydrogen, when hydrochloric acid is decomposed, are examples of this kind of reaction.

LAWS OF CHEMICAL ACTION

63. Law of Definite Proportions.—The different subjects so far considered in connection with chemical combinations all tend to prove the fact that chemical reactions are based on definite principles to which there are no exceptions. The subjects of atomic weights, valence, and the number of atoms reacting all lead to the general principle that there is a definite and fixed way in which different quantities of elements combine to form new substances.

Consider, for example, the compound magnesium oxide, MgO, resulting from the union of magnesium, Mg, and oxygen, O. The atomic weight of magnesium is, according to Table III, 24.32 and that of oxygen is 16. The molecular weight of magnesium oxide is equal to the sum of the atomic weights of magnesium and oxygen, or $24.32+16.0=40.32$. These figures show that every 40.32 parts by weight of magnesium oxide contain 24.32 parts by weight of magnesium and 16 parts by weight of oxygen. Investigations of magnesium oxide, no matter in what way the substance may have been made, show that these relative weights are always the same; that there is never any ratio between magnesium and oxygen other than 24.32 : 16. A ratio between two terms, such as x and y, is generally expressed as $x : y$, in which x and y are the values being compared; it is read: x to y. The ratio may also be written as a fraction, $\frac{x}{y}$.

Magnesium and oxygen being divalent, 1 atom of each is contained in magnesium oxide. The ratio of the number of magnesium atoms to the number of oxygen atoms has never been found to be other than 1 : 1; neither have any elements other than magnesium and oxygen ever been found in magnesium oxide.

The foregoing observations can be summed up in a general way by stating that each molecule of magnesium oxide always consists of 1 atom of magnesium and 1 of oxygen in the same proportion by weight. They verify the law of definite proportions, which states that a chemical compound always contains the same constituents in the same proportion by weight. This law forms a basis for every application of valence and of atomic weights. The principles of valence and of atomic weights are correctly used only when they are in accord with the aforementioned broad principle covered by the law of definite proportions.

64. Law of Multiple Proportions.—Some elements as shown in Table V have more than 1 valence and can combine with some other element to form more than one compound. Consider, for example, tin and chlorine. The former has valences of 2 and 4 and the latter a valence of 1 when combined with metals like tin. These elements form stannous chloride, $SnCl_2$, and stannic chloride, $SnCl_4$. By means of the atomic weights given in Table III, one is able to calculate the parts by weight of chlorine that unite with a fixed weight of tin. For instance, the atomic weight of tin is 118.7 and that of chlorine is 35.46. There are, in stannous chloride, $SnCl_2$, $35.46 \times 2 = 70.92$ parts by weight of chlorine to every 118.7 parts by weight of tin; likewise, there are, in stannic chloride, $SnCl_4$, $35.46 \times 4 = 141.84$ parts by weight of chlorine to every 118.7 parts by weight of tin. The parts by weight of chlorine combined in stannous chloride and stannic chloride, combined with 118.7 parts by weight of tin, bear a ratio to each other of 70.92 : 141.84. Reducing the terms of this ratio to their lowest values by dividing by 70.92, the ratio becomes 1 : 2. This ratio is called a simple one, because it can be expressed in whole numbers.

The foregoing illustration is an example of the law of multiple proportions, which may be stated as follows: *When two elements combine to form more than one compound, the weights of the one that unite with a fixed weight of the other bear a simple ratio to each other.*

NOMENCLATURE

NAMES OF CHEMICAL COMPOUNDS

ACIDS, BASES, AND SALTS

65. General Remarks.—In the early days of the development of chemical science, names were applied to substances without following any fixed plan. Recently, however, when the chemical composition of nearly every substance is known, substances referred to in chemistry are named according to a plan in which the chemical composition of the substance plays the most important part. No one can consider his education in chemistry satisfactory, unless he thoroughly understands the system followed in naming substances and knows how to apply it. One should know the proper use of names like acid, base, salt, peroxide, sulphide, chlorate, chlorite, and many other terms. The following explanation of this subject should be considered carefully, for it treats of the definitions and rules upon which the naming of substances is based and is applicable to every branch of inorganic chemistry.

66. Acids.—It is well to consider some of the acids to determine whether there are any specific characteristics that distinguish them from all other substances. Sulphuric acid and hydrochloric acid are two substances used a great deal by chemists and their formulas, H_2SO_4 and HCl, respectively, show that they both contain hydrogen, but so do many other substances that are not acids, as, for example, calcium hydroxide, $Ca(OH)_2$, potassium hydroxide, KOH, and water, H_2O. How does the hydrogen in acids, therefore, differ from the hydrogen in other substances?

Acids, when allowed to act on metals, as, for example, zinc or iron, chemically combine with them and hydrogen is set free.

Following is the reaction that takes place when zinc reacts with each acid mentioned:

$$Zn+2HCl=ZnCl_2+H_2$$
$$Zn+H_2SO_4=ZnSO_4+H_2$$

In the first case, zinc chloride and hydrogen are formed; in the second, zinc sulphate and hydrogen are the products of the reaction. It has been found by experiment that acids are the only substances of those containing hydrogen that can react with metals or equivalent elements to form the products hydrogen and salts. Therefore, acids contain hydrogen that can be replaced by metals.

It has also been found that acids can change the color of litmus, a vegetable dye of indefinite chemical composition, from blue to red.

From the foregoing facts, it is obvious that acids have distinct characteristics possessed by no other class of substances, and that the following definition will apply: *An* **acid** *is any substance containing hydrogen which may be replaced by a metal and which will also change the color of litmus from blue to red.*

67. Bases and Alkalies.—By the term *base* is meant all metals, their oxides and hydroxides, which react with acids to produce compounds called *salts*. An *alkali* is a particular kind of base in that its aqueous solution will change the color of red litmus to a blue. Thus, according to the foregoing definitions, the following metals, oxides and hydroxides are bases but they are not alkalies: Copper, Cu; cupric oxide, CuO; cupric hydroxide, $Cu(OH)_2$; iron, Fe; ferric oxide, Fe_2O_3; ferric hydroxide, $Fe(OH)_3$; manganese, Mn; manganese dioxide, MnO_2; and manganous hydroxide, $Mn(OH)_2$. As illustrations of metals, their oxides and hydroxides, that are alkalies as well as bases, the following will serve: Sodium, Na; sodium oxide, Na_2O; sodium hydroxide, $NaOH$; potassium, K; potassium oxide, K_2O; potassium hydroxide, KOH; ammonium hydroxide, NH_4OH; barium, Ba; barium oxide, BaO and barium hydroxide, $Ba(OH)_2$.

68. Metals and Non-Metals.—Elements that form basic hydroxides and can replace hydrogen in acids are called **metals.**

They all have what is known as a metallic luster, when in compact form. In powdered form, however, most of them appear black. For example, magnesium, a metal that is lustrous in compact form, is gray when powdered.

Non-metals have neither a metallic luster nor do they replace hydrogen in acids. Their oxides and hydroxides generally give acid reactions. In combination with hydrogen or hydrogen and oxygen, they all form acids.

The dividing line between metals and non-metals is, however, not a sharp one, for some elements can act either as metals or non-metals, depending on the conditions. For example, silicon appears as a metal in silicon disulphide, SiS_2, and as a non-metal in metasilicic acid, H_2SiO_3. Elements that commonly act both as metals and non-metals are called **metalloids.** Metals are called *positive elements* and non-metals *negative elements*, based on their action during *electrolysis*.

Table VII shows the divisions into which the important elements are conveniently grouped. It should be borne in mind, however, that the classification is somewhat arbitrary, for some elements classed as metals will under certain conditions act as non-metals. For example, aluminum ordinarily acts as a metal; yet, when its compounds react chemically with sodium hydroxide, they form sodium aluminate, in which substance aluminum acts as a non-metal, thus:

$$2Al(OH)_3+2NaOH=Na_2Al_2O_4+4H_2O$$

69. Neutralization.—A neutral solution of the vegetable dye litmus is blue in color. As previously stated, solutions of acids have the power of changing this color to red and solutions of bases in water have the power of restoring the blue color. For example, if 2 or 3 drops of hydrochloric acid are added to a neutral litmus solution, the color of the solution will be changed to a bright red. If, now, a few drops of a solution of sodium hydroxide in water are added to the reddened litmus solution, the original blue color will be restored. By adding sufficient acid, the color of the solution may again be changed to red. When the red color is obtained, the solution is said to show an acid

TABLE VII

METALS AND NON-METALS

Metals		Non-Metals
Names	Names	Names
Aluminum	Neodymium	Argon
Antimony	Nickel	Arsenic
Bismuth	Osmium	Boron
Cadmium	Palladium	Bromine
Cæsium	Platinum	Carbon
Calcium	Potassium	Chlorine
Cerium	Praseodymium	Fluorine
Chromium	Radium	Helium
Cobalt	Rhodium	Hydrogen
Columbium	Rubidium	Iodine
Copper	Ruthenium	Krypton
Dysprosium	Scandium	Neon
Erbium	Sodium	Niton
Europium	Silver	Nitrogen
Gallium	Strontium	Oxygen
Gadolinium	Tantalum	Phosphorus
Germanium	Terbium	Selenium
Glucinum	Thallium	Silicon
Gold	Thorium	Sulphur
Holmium	Thulium	Tellurium
Indium	Tin	Xenon
Iridium	Titanium	
Iron	Tungsten	
Lanthanum	Uranium	
Lead	Vanadium	
Lithium	Ytterbium	
Magnesium	Yttrium	
Manganese	Zinc	
Mercury	Zirconium	
Molybdenum		

reaction, and when the blue color is restored, it shows an alkaline reaction. If the acid is very carefully added to the blue solution, the blue color will become less distinct at a certain point, and the solution, while still blue, will be found to have a slight reddish tint. At about this point the solution is neutral; that is, it is neither basic nor acid, the base and acid having neutralized, or destroyed, the properties of each other. This process of destroying basic and acid properties by allowing a base and acid to act on each other is known as *neutralization.*

The question now arises: Is a definite amount of acid required to neutralize a fixed amount of base? That this is a fact may easily be shown by experiments and it is upon this principle that one of the branches of analytical chemistry is based.

70. As an example, if two solutions are made up, one containing sulphuric acid, H_2SO_4, and the other sodium hydroxide, $NaOH$, and a quantity of the acid solution is added to a quantity of the alkaline solution containing a few drops of a solution of litmus, until the blue color of the litmus just changes to a red, the solution will be about neutral. The quantities of alkali and acid solutions used are then noted and a second experiment performed, using the solutions in the same proportion but in different quantities and it will be found, in each case, that a certain quantity of the acid will neutralize a certain quantity of the alkali.

71. At this point it will not be out of place to call attention to the fact that most but not all reactions in inorganic chemistry take place quantitatively or, theoretical quantities as indicated by equations representing the reactions, are actually obtained. For the sake of clearness, an example will be given.

In the reaction between zinc and hydrochloric acid,

$$\overset{65.37}{Zn} + \overset{72.936}{2HCl} = \overset{136.29}{ZnCl_2} + \overset{2.016}{H_2}$$

if molecular quantities of zinc and hydrochloric acid are used, molecular quantities of zinc chloride and hydrogen will be obtained; that is, if 65.37 pounds of zinc are acted upon by 72.936 pounds of hydrochloric acid, 136.29 pounds of zinc chloride and 2.016 pounds of hydrogen will be obtained. This

is known as a theoretical yield of product or the reaction is said to proceed quantitatively. However, it will be shown later in organic chemistry, that a theoretical yield of product is the exception rather than the rule. In other words, when a reaction proceeds up to a certain point, it stops.

72. Salts.—The term **salt** is ordinarily applied to sodium chloride. In chemistry, however, it refers to the products formed when the hydrogen atoms of acids have been replaced by metals. The majority of substances included in inorganic chemistry come under this heading. To illustrate the formation of a salt: Zinc reacts with sulphuric acid to form hydrogen and the salt zinc sulphate; thus,

$$Zn+H_2SO_4=ZnSO_4+H_2$$

The metal portion of a salt, in this case zinc, is called the positive radical, and the acid portion with which the metal is combined, in this case SO_4, is called the negative radical. The negative radical of an acid is always the portion of the acid that combines with hydrogen. For example, the negative radical of nitric acid, HNO_3, is NO_3. A negative radical must be combined with a positive radical before its valence is satisfied.

Salts are commonly prepared by treating a base with an acid, and as a result of the reaction which takes place water is also produced. For example, potassium hydroxide and hydrochloric acid react to form the salt potassium chloride and water, thus:

$$KOH+HCl=KCl+H_2O$$

Potassium chloride is found to have neither the basic properties of potassium hydroxide nor the acid properties of hydrochloric acid; in fact, it does not affect litmus in any way. It is a neutral substance so far as acid or basic properties are concerned.

73. Normal, Acid, Basic, and Mixed Salts.—The salts so far considered are those in which just enough metal is supplied to replace the hydrogen atoms in an acid; but there are other kinds. The following distinctions must, therefore, be made: A *normal salt* is a salt obtained from an acid by replac-

ing all its hydrogen atoms by metal atoms. An **acid salt** is a salt obtained from an acid by replacing part of the hydrogen atoms by metal atoms. A **basic salt** is a salt obtained by the partial neutralization of a base by an acid. Following are equations showing the processes as used to produce the different kinds of salts:

A normal salt:

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O$$

The resulting potassium sulphate, K_2SO_4, is a normal salt, for all the hydrogen atoms in the acid have been replaced by potassium atoms.

An acid salt:

$$KOH + H_2SO_4 = KHSO_4 + H_2O$$

The resulting potassium hydrogen sulphate, $KHSO_4$, is an acid salt, for all the hydrogen atoms in the acid have not been replaced by potassium atoms.

A basic salt:

$$Zn(OH)_2 + HCl = Zn(OH)Cl + H_2O$$

The resulting zinc hydroxy-chloride is a basic salt, for the base has been only partly neutralized by the acid.

74. A **mixed salt** differs from a normal salt in that the hydrogen atoms in the acid have been replaced by two or more metals. For example, the mixed salt sodium potassium sulphate, $KNaSO_4$, can be made by first producing the acid salt potassium hydrogen sulphate and then treating this with sodium hydroxide, thus:

$$KOH + H_2SO_4 = KHSO_4 + H_2O$$
$$KHSO_4 + NaOH = KNaSO_4 + H_2O$$

A mixed salt, also called a double salt, is formed by the replacement of the hydrogen atoms in an acid by different metals.

ACID SALTS, BASIC ACIDS, AND ACID BASES

75. Nomenclature of Acid Salts.—Different names are applied to acid salts in accordance with the number of hydrogen atoms that have been replaced by metals. For example, phosphoric acid, H_3PO_4, can form three kinds of salts

with sodium, depending on the number of sodium atoms that enter into the compound. Following are reactions showing the formation of the three salts formed by the action of phosphoric acid on sodium hydroxide:

$$NaOH + H_3PO_4 = NaH_2PO_4 + H_2O$$
$$2NaOH + H_3PO_4 = Na_2HPO_4 + 2H_2O$$
$$3NaOH + H_3PO_4 = Na_3PO_4 + 3H_2O$$

The salt having the formula Na_3PO_4 is called normal sodium phosphate, because all of the hydrogen atoms in the acid have been replaced by sodium atoms. The other two salts formed, Na_2HPO_4 and NaH_2PO_4, are acid salts, because only part of the hydrogen atoms in the acid have been replaced by sodium atoms. Different names must be applied to them so that they can be distinguished from each other.

76. Based on the number of sodium atoms in the various salts, the following system of naming them is used:

NaH_2PO_4 = monosodium phosphate
Na_2HPO_4 = disodium phosphate
Na_3PO_4 = trisodium phosphate

Based on the number of hydrogen atoms in the various salts, the following system of names is used:

NaH_2PO_4 = dihydrogen sodium phosphate
Na_2HPO_4 = monohydrogen sodium phosphate
Na_3PO_4 = normal sodium phosphate

Following is another set of names that is sometimes used:

NaH_2PO_4 = primary sodium phosphate
Na_2HPO_4 = secondary sodium phosphate
Na_3PO_4 = tertiary sodium phosphate

The name sodium phosphate is usually applied to Na_2HPO_4, for this salt is the most common of the three.

77. Some acids, like sulphuric acid, form but one acid salt with a metal. For example, potassium hydroxide can react with sulphuric acid in the following ways:

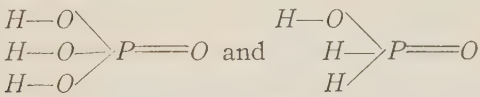
$$KOH + H_2SO_4 = KHSO_4 + H_2O$$
$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O$$

The normal salt, K_2SO_4, is called potassium sulphate. The acid salt is called acid potassium sulphate or potassium hydrogen sulphate. No other names are necessary, as in the case of the sodium phosphates, for there is but one acid potassium sulphate. Acid potassium sulphate is sometimes called potassium bisulphate or potassium disulphate to show that twice as much SO_4 radical is present as is needed to form a normal salt with the potassium contained.

78. Basicity of Acids.—All the hydrogen atoms in the acids so far considered can be replaced by metals. There are a few acids, however, in which only a part of the hydrogen atoms can be replaced, and in order to explain more clearly why only certain of the hydrogen atoms are replaced, graphic or structural formulas, in which the valence of the different atoms is indicated by means of dashes, will be used.

Consider the two oxyacids (acids containing oxygen), phosphoric acid, H_3PO_4, and hypophosphorous acid, H_3PO_2. Investigation in the laboratory has shown that although phosphoric and hypophosphorous acids each contain 3 hydrogen atoms, only 1 of these in hypophosphorous acid may be replaced by a metal. The graphic or structural formulas of these acids are, respectively:

phosphoric acid hypophosphorous acid



In these formulas the valence of each atom is indicated as follows: Hydrogen is always monovalent in any compound, therefore each hydrogen atom is shown, connected by one bond, or dash, to an oxygen or phosphorus atom. Oxygen is always bivalent and each atom is therefore shown connected once to hydrogen and once to phosphorus, thus satisfying its valence of 2. In each formula, however, one oxygen atom must be written with a double bond in order to show its valence of 2. Phosphorus in phosphoric acid is pentavalent and is shown connected twice to one oxygen and once to each of three oxygens, thus satisfying its valence of 5. The 3 hydrogen atoms of

phosphoric acid are replaceable; the graphic formula is therefore written to show that each hydrogen atom is directly connected to oxygen, but only 1 of the hydrogen atoms of hypophosphorous acid is replaceable. The first acid contains three hydroxyl, *OH*, groups and the latter but one. Investigations showed that only hydrogen atoms in the hydroxyl groups of oxyacids are replacable by metals and that those hydrogen atoms of oxyacids that are not in the hydroxyl groups are not replaceable by metals. These facts do not, of course, apply to acids that do not contain oxygen. The hydrogen atoms in acids like hydrochloric acid, *HCl*, and hydrofluoric acid, *HF*, can be entirely replaced by a metal.

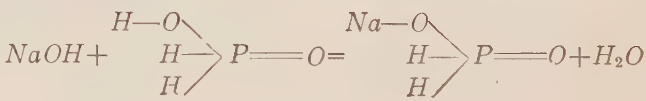
79. An acid that requires 1 atom of a monovalent metal to replace all the replaceable hydrogen in 1 molecule of it is said to be a monobasic acid. An acid that requires 2 atoms of a monovalent metal or 1 atom of a divalent metal to replace all the replaceable hydrogen in 1 molecule of it is said to be dibasic. An acid that requires 3 atoms of a monovalent metal or 1 atom of a trivalent metal to replace all of the replaceable hydrogen in 1 molecule of it is said to be tribasic. The basicity of an oxyacid, as shown before, is limited by the number of hydroxyl groups it contains; all the hydrogen atoms in acids that do not contain oxygen are replaceable by metals. The term *basicity* is used because the metals that replace the hydrogen in acids are usually obtained from bases.

80. Examples of Reactions Between Bases and Acids.—The following examples will serve to make the conception of the basicity of acids clear:

Monobasic acids:

(*a*) $NaOH + HCl = NaCl + H_2O$

Hydrochloric acid is monobasic because 1 molecule of the base, sodium hydroxide, is needed to supply the 1 atom of monovalent sodium required to replace the hydrogen atom in one of its molecules.

(*b*) 

Hypophosphorous acid is monobasic because 1 molecule of the base, sodium hydroxide, is needed to supply the 1 atom of monovalent sodium required to replace the replaceable hydrogen atom in 1 molecule of it.

Diabasic acids:

(*a*) $$2KOH+H_2SO_4=K_2SO_4+2H_2O$$

Sulphuric acid is dibasic because 2 molecules of the base, potassium hydroxide, are needed to supply the 2 atoms of monovalent potassium required to replace the replaceable atoms of hydrogen in 1 molecule of it.

(*b*) $$Ca(OH)_2+H_2SO_4=CaSO_4+2H_2O$$

Sulphuric acid is shown to be dibasic by this reaction also, because 1 molecule of the base, calcium hydroxide, is needed to supply the 1 atom of divalent calcium required to replace the replaceable hydrogen atoms in 1 molecule of it.

Tribasic acids:

(*a*) $$3NaOH+H_3PO_4=Na_3PO_4+3H_2O$$

Phosphoric acid is tribasic because 3 molecules of the base, sodium hydroxide, are needed to supply the 3 atoms of univalent sodium required to replace the replaceable hydrogen atoms in 1 molecule of it.

(*b*) $$Al(OH)_3+H_3PO_4=AlPO_4+3H_2O$$

Phosphoric acid is shown to be tribasic by this reaction also, because 1 molecule of the base, aluminum hydroxide, is needed to supply the 1 atom of trivalent aluminum required to replace the replaceable hydrogen atoms in 1 molecule of it.

81. **Acidity of Bases.**—Bases are classed according to the number of hydrogen atoms that can be replaced in an acid by 1 atom of the metal supplied. For example, sodium hydroxide, $NaOH$, is a monacid base, because each molecule of it supplies 1 atom of monovalent sodium, capable of replacing 1 hydrogen atom in an acid. Calcium hydroxide, $Ca(OH)_2$, is a diacid base, because each molecule of it supplies 1 atom of divalent calcium, capable of replacing 2 hydrogen atoms in an acid. Aluminum hydroxide, $Al(OH)_3$, is a triacid base. because each molecule

of it supplies 1 atom of trivalent aluminum, capable of replacing 3 hydrogen atoms in an acid. The reactions used to exemplify the basicity of acids should be studied in connection with the acidity of bases, for they show how monacid, diacid, and triacid bases react with acids.

COMPOUNDS CONTAINING TWO ELEMENTS

82. Binary Compounds.—Compounds that consist of two elements, or two groups acting as elements, are called *binary compounds.* The ending *ide* is applied to these substances. In Table VIII are shown a few examples of binary compounds and the system of naming them. In each case, the ending *ide* is applied to the less positive or the negative elements; usually, a non-metal. The more positive element, usually a metal, is written before the less positive or negative element.

TABLE VIII

NOMENCLATURE OF BINARY COMPOUNDS

Positive Element	Negative Element	Formula	Name of Binary Compound
Magnesium	Oxygen	MgO	Magnesium oxide
Zinc	Sulphur	ZnS	Zinc sulphide
Potassium	Bromine	KBr	Potassium bromide
Calcium	Carbon	CaC_2	Calcium carbide
Sodium	Chlorine	$NaCl$	Sodium chloride
Hydrogen	Sulphur	H_2S	Hydrogen sulphide
Hydrogen	Chlorine	HCl	Hydrogen chloride
Lead	Iodine	PbI_2	Lead iodide
Ammonium	Chlorine	NH_4Cl	Ammonium chloride

83. In some cases an element can unite with another element to form more than one compound. There is a system of naming these substances so that they can be distinguished from one another. For example, iron may unite with chlorine to form two different kinds of chlorides, depending on the number

of atoms of chlorine joined to 1 atom of iron; or, depending on the valence of the iron in each chloride. The chloride $FeCl_2$, in which iron is divalent and in which but 2 atoms of chlorine are present to every atom of iron, is called ferrous chloride. The substance $FeCl_3$, in which iron is trivalent and in which 3 atoms of chlorine are present to every atom of iron, is called ferric chloride. In other words, the ending *ous* is added to the name of the positive element, usually a metal, to show that it is present with the lower valence and that it is combined with a lower amount of negative element than in the compound in which the positive element has the ending *ic*.

Following are a few examples showing the use of the endings *ous* and *ic:*

Cu_2O, cupr*ous* oxide	CuO, cupr*ic* oxide
$SnCl_2$, stann*ous* chloride	$SnCl_4$, stann*ic* chloride
Cr_2O_3, chrom*ous* oxide	CrO_3, chrom*ic* oxide

84. Elements Uniting in More Than One Proportion. Another method, in which a prefix is attached to the negative element, is used to distinguish binary compounds formed by elements uniting in more than one proportion. The prefixes *mono; di*, or *bi; tri; tetra;* and *penta* are applied to show whether the number of atoms of the negative element present is, respectively, one, two, three, four, or five. Following are a few examples of this system:

CO, carbon monoxide	CO_2, carbon dioxide
SO_2, sulphur dioxide	SO_3, sulphur trioxide
PCl_3, phosphorus trichloride	PCl_5, phosphorus pentachloride
H_2O, hydrogen monoxide	H_2O_2, hydrogen dioxide

The prefix *per* is sometimes applied to the negative element to show that the greatest possible number of atoms of the negative element is present, thus:

H_2O_2, hydrogen peroxide, known also as hydrogen dioxide
PbO_2, lead peroxide, known also as lead dioxide
Na_2O_2, sodium peroxide, known also as sodium dioxide

There is no compound of hydrogen and oxygen in which there is a greater proportion of the negative element than in

hydrogen peroxide. The same fact holds true for all other binary compounds in which the prefix *per* appears.

The following oxides of nitrogen are excellent examples of substances that follow the nomenclature explained in the foregoing:

N_2O, nitrous oxide
NO, nitric oxide
N_2O_3, nitrogen trioxide
NO_2 or N_2O_4, nitrogen dioxide or nitrogen tetroxide
N_2O_5, nitrogen pentoxide

The prefix *sesqui* is sometimes added to the negative element to denote that there is present $1\frac{1}{2}$ atoms of the negative element to every atom of the positive element. For example, Fe_2O_3, ferric oxide, is sometimes called iron sesquioxide.

NOMENCLATURE OF ACIDS AND SALTS BELONGING TO ONE SERIES

85. Series of Acids.—The system of naming acids and salts should be studied carefully, for it is used in every phase of chemistry. Some acids so far considered have names ending in *ic*. Others end in *ic*, but have in addition the prefix *hydro;* others, again, have different prefixes and suffixes. Each one of them is, however, based on the same system of naming substances.

An acid is generally named by referring to its characteristic element. It should be borne in mind, however, that in an acid neither hydrogen nor oxygen can be considered as a characteristic element, for the former is found in all and the latter in most acids. For example, H_2SO_4 is called sulphuric acid, and HNO_3, nitric acid, being named with reference to the respective characteristic elements sulphur and nitrogen.

The principal acid of a series takes the ending *ic*, as $HClO_3$, chloric acid; the next acid in the series, containing less oxygen than the principal acid, takes the ending *ous*, as $HClO_2$, chlorous acid; the acid containing even less oxygen than the acid ending in *ous*, takes the ending *ous* and the prefix *hypo*, as $HClO$, hypochlorous acid; the acid of the series containing hydrogen

and the characteristic element only, takes the ending *ic* and the prefix *hydro*, as *HCl*, hydrochloric acid. If there is an acid in the series containing more oxygen than the principal acid, it has the ending *ic* and the prefix *per*, as $HClO_4$, perchloric acid.

Following is a summary of the formulas and names of the acids of chlorine:

HCl, *hydro*chlor*ic* acid
HClO, *hypo*chlor*ous* acid
$HClO_2$, chlor*ous* acid
$HClO_3$, chlor*ic* acid
$HClO_4$, *per*chlor*ic* acid

86. The foregoing names have been used for years. There is also a set of names based on scientific grounds, that can properly be used to designate the various chlorine acids, as follows:

HCl, hydrogen chlor*ide*
HClO, hydrogen *hypo*chlor*ite*
$HClO_2$, hydrogen chlor*ite*
$HClO_3$, hydrogen chlor*ate*
$HClO_4$, hydrogen *per*chlor*ate*

87. Series of Salts.—The names of salts depend on the names of the acids from which they are formed. A salt formed by a metal and the negative radical of an oxyacid ending in *ic* has the ending *ate;* and a salt consisting of a metal and the negative radical of an oxyacid ending in *ous* has the ending *ite*. The prefix appearing in the name of the acid is retained in the name of the salt. As has been explained before, names of salts consisting of but two elements end in *ide*, even though the acid has the prefix *hydro* and the suffix *ic*. Names of salts of chlorine acids receive the same endings as the acids, as shown in the foregoing explanations, excepting that the name of the metal in the salt is used instead of hydrogen. Following are the names of different salts formed when potassium hydroxide reacts with the acids of chlorine:

KCl, potassium chlor*ide*; formed from *HCl*, *hydro*chlor*ic* acid.

KClO, potassium *hypo*chlor*ite*; formed from *HClO*, *hypo*-chlor*ous* acid or hydrogen *hypo*chlor*ite*.

$KClO_2$, potassium chlor*ite*; formed from $HClO_2$, chlor*ous* acid or hydrogen chlor*ite*.

$KClO_3$, potassium chlor*ate*; formed from $HClO_3$, chlor*ic* acid or hydrogen chlor*ate*.

$KClO_4$, potassium *per*chlor*ate*; formed from $HClO_4$, *per*-chlor*ic* acid or hydrogen *per*chlor*ate*.

88. Salts containing positive elements that exhibit more than one valence are named in much the same way as binary compounds containing positive elements that have more than one valence. The name of the positive element, when it has the lower valence, takes the ending *ous*, and when it has the higher valence, takes the ending *ic*. Thus:

$SnSO_4$, stannous sulphate
$Sn(SO_4)_2$, stannic sulphate

Each salt is a sulph*ate*, for each one of them contains the negative radical, SO_4, of sulphur*ic* acid. The salt in which tin is divalent is called stann*ous* sulphate, and the one in which it is tetravalent is called stann*ic* sulphate.

89. Formulas and Names of Some Common Acids and Salts.—The following examples of acids and their salts are given in order to further illustrate the general application of the nomenclature explained in the preceding pages:

Acids	Sodium Salts
Hydrochlor*ic* acid, HCl	Sodium chlor*ide*, $NaCl$
Sulphur*ous* acid, H_2SO_3	Sodium sulph*ite*, Na_2SO_3
Sulphur*ic* acid, H_2SO_4	Sodium sulph*ate*, Na_2SO_4
Nitr*ous* acid, HNO_2	Sodium nitr*ite*, $NaNO_2$
Nitr*ic* acid, HNO_3	Sodium nitr*ate*, $NaNO_3$
Phosphor*ous* acid, H_3PO_3	Sodium phosph*ite*, Na_2HPO_3
Phosphor*ic* acid, H_3PO_4	Sodium phosph*ate*, Na_3PO_4

Miscellaneous Salts and Compounds

Cupr*ous* oxide, Cu_2O
Cupr*ic* oxide, CuO
Mercur*ic* chloride, or mercury *bi*chlor*ide*, $HgCl_2$
Mercur*ous* chlor*ide*, $HgCl$

Ferr*ous* sulph*ate*, $FeSO_4$
Ferr*ic* sulph*ate*, $Fe_2(SO_4)_3$
Ferr*ous* sulph*ite*, $FeSO_3$
Ferr*ic* sulph*ite*, $Fe_2(SO_3)_3$
Sodium *per*chlor*ate*, $NaClO_4$
Stann*ous* chlor*ide*, $SnCl_2$
Calcium chlor*ate*, $Ca(ClO_3)_2$
Sulphur *di*ox*ide*, SO_2
Sulphur *tri*ox*ide*, SO_3
Cupr*ous* sulph*ide*, Cu_2S
Cupr*ic* sulph*ide*, CuS

Sodium *bi*sulph*ate*, acid sodium sulph*ate*, or sodium hydrogen sulph*ate*, $NaHSO_4$

Acid sodium carbon*ate*, sodium hydrogen carbon*ate*, or sodium *bi*carbon*ate*, $NaHCO_3$

Potassium cyan*ide*, KCN
Calcium *hypo*chlor*ite*, $Ca(ClO)_2$

INORGANIC CHEMISTRY
(PART 2)

CHEMICAL THEORY—(Continued)

METHODS AND UNITS OF MEASUREMENT

METRIC WEIGHTS AND MEASURES

1. Fundamental Units.—The metric system is commonly used by chemists for expressing quantities by weight and volume.

In this system the fundamental unit of length is the meter, equal to 39.37 inches, and from it are derived the units of

TABLE I

PREFIXES OF THE METRIC SYSTEM UNITS

Prefixes and Unit	Meaning of Prefixes	Names of Units
milli-	one-thousandth $= \frac{1}{1000} = .001$	
centi-	one-hundredth $= \frac{1}{100} = .01$	
deci-	one-tenth $= \frac{1}{10} = .1$	*meter* (for length)
unit	one, or 1	*gram* (for weight)
deka-	ten, or 10	*liter* (for capacity)
hecto-	one hundred, or 100	
kilo-	one thousand, or 1000	

capacity and weight, called respectively the *liter* and the *gram*. All other units of the metric system are decimal subdivisions and multiples of these fundamental units; that is, they are

tenths, hundredths, etc., and ten times, one hundred times, etc., the meter, liter, and gram.

The meter, liter, and gram bear a simple relation to one another for 1,000 cubic centimeters are equal in capacity to that of 1 liter, and 1 liter of pure water at 4° C. weighs 1,000 grams.

2. Abbreviations of Units.—The following abbreviations are used to represent the various units:

M. = meter	kg. = kilogram
dm. = decimeter	gm. = gram
cm. = centimeter	dg. = decigram
mm. = millimeter	mg. = milligram
L. = liter	dl. = deciliter

TABLE II

MEASURES OF LENGTH, SURFACE, VOLUME, CAPACITY, AND WEIGHT

MEASURES OF LENGTH

10 millimeters (mm.) = 1 centimeter (cm.)
10 centimeters = 1 decimeter (dm.)
10 decimeters = 1 meter (M.)
10 meters = 1 dekameter (dkm.)
10 dekameters = 1 hectometer (hm.)
10 hectometers = 1 kilometer (km.)

MEASURES OF SURFACE

100 square millimeters (sq. mm. or mm^2.) = 1 square centimeter (sq. cm. or cm^2.)
100 square centimeters = 1 square decimeter (sq. dm. or dm^2.)
100 square decimeters = 1 square meter (sq. m. or m^2.)

MEASURES OF VOLUME

1,000 cubic millimeters (cmm. or mm^3.) = 1 cubic centimeter (ccm., c. c., or cm^3.)
1,000 cubic centimeters = 1 cubic decimeter (cdm. or dm^3.)
1,000 cubic decimeters = 1 cubic meter (m^3.)

MEASURES OF CAPACITY

10 milliliters (ml.) = 1 centiliter (cl.)
10 centiliters = 1 deciliter (dl.)
10 deciliters = 1 liter (L.)
10 liters = 1 dekaliter (dkl.)
10 dekaliters = 1 hectoliter (hl.)
10 hectoliters = 1 kiloliter (kl.)

MEASURES OF WEIGHT

10 milligrams (mg.) = 1 centigram (cg.)
10 centigrams = 1 decigram (dg.)
10 decigrams = 1 gram (gm.)
10 grams = 1 dekagram (dkg.)
10 dekagrams = 1 hectogram (hg.)
10 hectograms = 1 kilogram (kg.)
1,000 kilograms = 1 ton (t.)

3. Metric Units Commonly Used by Chemists.—The following table includes practically all of the weights and measures of the metric system that are commonly used by the chemist.

TABLE III

FUNDAMENTAL UNITS EMPLOYED BY CHEMISTS

1,000 cubic centimeters (c. c.) = 1 liter (L.)
1,000 grams (gm.) = 1 kilogram (kg.)
1,000 millimeters (mm.) = 1 meter (M.)

4. Metric and English Units Conversion Factors. The following factors are often used to convert measures and weights of one system into terms of another:

Pounds avoirdupois × .4536 = kilograms.
Ounces avoirdupois × 28.35 = grams.
Kilograms × 2.2046 = pounds avoirdupois.
Grams × .035274 = ounces avoirdupois.
Pounds Troy × .3732 = kilograms.
Kilograms × 2.6792 = pounds Troy.
Ounces Troy × 31.103 = grams.
Grams × .032151 = ounces Troy.
Grams × 15.432 = grains.
Grains × .0648 = grams.
Pounds per cubic inch × 27.7 = grams per cubic centimeter.
Pounds per cubic foot × 16.02 = kilograms per cubic meter.
Grams per cubic centimeter × .0361 = pounds per cubic inch.
Milligrams per liter = parts per million.
Grains per U. S. gallon × 17.138 = parts per million.
Parts per million × .583 = grains per U. S. gallon.
Gallons × 3.7854 = liters.
Liters × .26417 = gallons.

Liters $\times$ 1.0567 = liquid quarts.
Liquid quarts $\times$ .94636 = liters.
Liters $\times$ .9081 = dry quarts.
Dry quarts $\times$ 1.101 = liters.
Fluid ounces $\times$ 29.57 = cubic centimeters.
Cubic centimeters $\times$ .0338 = fluid ounces.
Meters $\times$ 1.09361 = yards.
Yards $\times$ .914402 = meters.
Centimeters $\times$ .3937 = inches.
Inches $\times$ 2.54001 = centimeters.
Miles $\times$ 1.60935 = kilometers.
Cubic feet $\times$ 28.32 = liters.

MEASUREMENT OF TEMPERATURE

5. Thermometers.—Chemists use instruments to measure the intensity of heat, that is, temperature, as heat has a strong influence on chemical action. Based on the fact that heat causes substances to expand, an instrument, called a *thermometer*, is constructed to measure temperatures. The substance used in it, usually mercury, is sensitive to heat changes and affords a means of determining the temperature. The mercury in the tube of the thermometer, Fig. 1, expands and rises as the temperature increases, and contracts and falls as the temperature decreases. While thermometers differ in construction and materials, they are based on the same principle.

6. Temperature Scales.—Thermometers are marked off into divisions, as shown in Fig. 1, each of which is called a *degree* and is expressed as 1°. The ordinary house thermometer, generally used in the United States, is based on the Fahrenheit scale. In this scale, the freezing point of pure water is called 32° F. and the boiling point 212° F. The space between the 32° F. and the 212° F. is divided into 180 equal parts, each one of which is called a degree Fahrenheit, expressed as 1° F. The scale is usually extended below and above 32° F. and 212° F., respectively, using the same divisions.

In the centigrade scale, generally used by chemists, the freezing point of water is called 0° C. and the boiling point 100° C. The divisions representing degrees are secured by dividing the space between 0° C. and 100° C. into 100 equal parts; these divisions are also extended below 0° C. and above 100° C.

7. It is frequently necessary to change from one scale to the other, in which case the following two rules are observed:

Rule I.—*To change from Fahrenheit to centigrade, subtract 32 from the temperature, Fahrenheit, multiply the result by 5, and divide by 9.*

Rule II.—*To change from centigrade to Fahrenheit, multiply the temperature, centigrade, by 9; divide the result by 5, and add 32.*

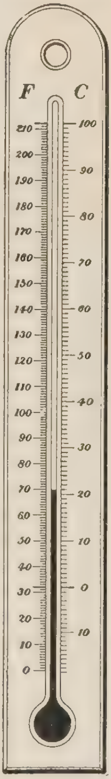


FIG. 1

EXAMPLE 1.—Convert 41° F. to its corresponding centigrade temperature.

SOLUTION.—Applying rule I, $41-32=9$; $9\times5=45$; $45\div9=5$. Hence 41° F. corresponds to 5° C. Ans.

EXAMPLE 2.—Convert 10° C. to its corresponding Fahrenheit temperature.

SOLUTION.—Applying rule II, $10\times9=90$; $90\div5=18$; $18+32=50$. Hence, 10° C. corresponds to 50° F. Ans.

EXAMPLE 3.—Convert −14° C. into Fahrenheit temperature.

SOLUTION.—Applying rule II, $-14\times9=-126$; $-126\div5=-25.2$; $-25.2+32=6.8$° F. Ans.

EXAMPLE 4.—Convert −13° F. into centigrade temperature.

SOLUTION.—Applying rule I, $-13-32=-45$; $-45\times5=-225$; $-225\div9=-25$° C. Ans.

8. Absolute Temperatures.—The conclusion is reached, as a result of experiments, that heat is entirely absent from all matter at a temperature 273 degrees below 0° C., usually expressed as −273° C., which point is called *absolute zero*, and temperatures reckoned therefrom are termed *absolute temperatures*. The absolute temperature of a body can be calculated

by adding 273 degrees to the temperature of the body expressed in degrees centigrade. For example, 30° C. expressed in terms of absolute temperature, is 30°+273°, or 303°; likewise, −10° C. is −10°+273°, or 263 degrees absolute temperature. The value 273 is not used on the Fahrenheit scale.

MEASUREMENT OF PRESSURES

9. Barometers.—When the study of the properties of gases is taken up, pressures are used in the different problems involved and for the sake of clearness, one type of the instrument by which pressures are measured, called a *mercurial barometer*, will be described.

Fig. 2

By the mercurial barometer the pressure is indicated by the height of a column of mercury and the pressure is usually expressed in either inches or millimeters. In Fig. 2 the space *a* is almost completely exhausted or freed from air and vapor so that the column of mercury *b* will not be depressed. The space *c* has access to the atmosphere through a small opening *d*, and the pressure in this space is the same as that outside the tube. The pressure in *c* forces column *e* down and column *b* up. Manufacturers of these instruments graduate them either in inches or millimeters, so that they record pressures accurately. Normal pressure of the atmosphere at sea level and 0° C. is equal to the pressure exerted by a column of mercury 760 millimeters, or 29.922 inches, high. In chemistry, pressure is generally expressed in millimeters.

10. Ways of Expressing Pressure.—Several ways of expressing pressure are in use. One is based on the number of pounds exerted on a square inch of surface; another is based on the number of kilograms exerted on a square centimeter of surface; another on the height of a column of mercury, either in inches or millimeters; and still another on the height of a column of water, either in feet or inches. Table IV can be used to change the pressure expressed in terms of one system to those of another. For example, a pressure

of 5 pounds per square inch is equivalent to 5 times 2.0408, or 10.2040 inches of mercury; likewise 20 millimeters of mercury are equivalent to 10.68 inches of water.

TABLE IV

PRESSURE EQUIVALENTS

	Pounds per Sq. In.	Inches of Mercury	Mm. of Mercury	Feet of Water	Inches of Water	Kg. of Sq. Cm.
Pounds per sq. in.	1.00	2.0408	51.836	2.31	27.711	.070308
Inches of mercury	.49	1.00	25.4	1.133	13.596	.03445
Mm. of mercury.	.01929	.03937	1.00	.0445	.5340	.0013563
Inches of water..	.03608	.07355	1.868	.0833	1.00	.002537
Kgm. per sq. cm.	14.2232	29.0267	737.27	32.845	394.139	1.00

The phrase *under ordinary conditions of temperature and pressure*, which is frequently met in studying properties of gases, means 0° C. and 760 mm. As previously stated, a pressure of 760 mm. is equivalent to normal air pressure at sea level, which in turn is equivalent to 14.7 pounds per square inch. This pressure is usually designated as one atmosphere.

PROPERTIES OF GASES

11. Specific Gravity and Density.—Methods for the determination of the specific gravities of different substances have been properly taken up in the subject of *Physics* and only the difference between specific gravity and density, as the terms are applied to gases, will be considered here. *The specific gravity of any gas is its weight compared with the weight of an equal volume of air at the same temperature and pressure. The density of a gas, on the other hand, is its weight compared with the weight of an equal volume of hydrogen, under like conditions of temperature and pressure.* For example, it is found that oxygen is 1.106 times as heavy as an equal volume of air, and 15.87 times as heavy as an equal volume of hydrogen. The specific gravity of oxygen is, therefore, 1.106 (air = 1) and the density is 15.87 (hydrogen = 1).

12. Relation of Density to Molecular Weight. There is no definite relation between the density of a liquid or solid and its molecular weight, but a study of the molecular weights and densities of a few gases will show that there is a distinct mathematical relation between the densities and molecular weights of gases. Hydrogen has a molecular weight of 2.016 and a density of 1; the density is approximately one-half the molecular weight. The density of oxygen was found by experiment to be 15.87 and its molecular weight is 32.00; the density of oxygen is almost one-half its molecular weight. The density of nitrogen was found by tests to be 13.89 and its molecular weight 28.016; the density of nitrogen is nearly one-half its molecular weight. It is found that the densities of most gases are approximately equal to one-half their respective molecular weights. In solving chemical problems, the chemist often finds it more convenient to use one-half the molecular weight for the density than to look up the exact figures.

13. The Weight of One Liter of a Gas.—Upon investigation it has been determined that 1 liter of hydrogen at 0° C. and 760 mm. weighs .089873 gram. As the density of any gas is its weight compared with the weight of an equal volume of hydrogen, the weight of 1 liter of hydrogen, multiplied by the density of a gas, will be the weight of 1 liter of that gas. Hence, *.089873, multiplied by the density of a gas, gives the weight of 1 liter of that gas at 0° C. and 760 mm.* For approximate values, the density of most gases can be taken as one-half the molecular weight. This rule can be used only when the volume of a gas is at 0° C. and 760 mm.; if at any other temperature and pressure, certain corrections must be made which will be explained later when pressure and temperature effects on the volume of gases are treated.

KINETIC THEORY OF GASES

14. In a preceding Section, when discussing the different forms of matter, something was said about the theory regarding the movement of molecules. This theory is called the kinetic theory, since the word *kinetic* signifies motion, and, according to it, *the molecules of all matter, whether in the solid, liquid, or gaseous form, are in a state of constant motion.* In the case of a solid, the molecules are in such intimate contact with one another that great freedom of motion is prohibited; in other words, spaces between the molecules, or intermolecular spaces, do not exist to any extent. This explains why solids retain their various shapes and why they possess such low compressibility, since, according to the theory, it is not the molecules in any substance themselves which are compressed when the substance is subjected to great pressure, but the intermolecular spaces are lessened, causing a reduction in volume upon the application of pressure. But if intermolecular spaces hardly exist, as in the case of a solid, its low compressibility is easily explained. In the case of a liquid, the intermolecular spaces are slightly larger than those of a solid and this means that the molecules of the liquid are more free to move, and consequently a liquid quickly takes the shape of its container. The spaces between the molecules of a gas at ordinary temperature and pressure must be relatively very great, compared with the spaces between the molecules of a solid and liquid, and this accounts for the great compressibility of gases. The molecules of a gas are apparently in constant motion. They are traveling in straight lines in all directions, and are continually colliding with one another and with the walls of any containing vessel, and because of this bombardment of the walls of the containing vessel, a confined gas exerts a certain pressure. It is also assumed that, when the molecules of a gas collide, they rebound with the same velocity and energy as before. If this were not the case, they would soon lose their momentum and come to rest, and this would result in a decrease in pressure of a confined gas, which does not occur. Therefore, it is assumed that the molecules of a gas are perpetually in motion.

DIFFUSION

15. Diffusion of Solids, Liquids, and Gases.—If the molecules of all substances are in a constant state of motion, it is but natural to suppose that, if two different non-reacting substances in a pure state are brought together, their molecules will intermingle. That this is exactly what occurs, may be easily proved, and although, in the case of solids, the process takes place at a much slower rate than with liquids or gases, this is what might be expected according to the kinetic theory. But the molecules of solids are still in motion to the extent that carbon is known to mix with pure hot iron, and gold with lead. The time occupied, however, before any appreciable change takes place, is in most cases a matter of years.

With liquids of mutual solubility, mixing, or diffusion, takes place much more rapidly; thus, if glycerine is placed in contact with water, a homogeneous solution will soon result. It is in the case of gases, however, that the phenomenon of diffusion is most striking. Here it may be shown that, regardless of their specific gravities or densities, gases will mix, so that if the mouth of a 1-liter bottle containing hydrogen is inverted over the mouth of a 2-liter bottle containing carbon dioxide, part of the hydrogen will pass into the bottle containing carbon dioxide and part of the carbon dioxide will pass into the bottle containing hydrogen, until finally each bottle will contain 1 part by volume of hydrogen to 2 parts by volume of carbon dioxide. The 1-liter bottle will contain $\frac{1}{3}$ liter of hydrogen and $\frac{2}{3}$ liter of carbon dioxide; the 2-liter bottle will contain $\frac{2}{3}$ liter of hydrogen and $1\frac{1}{3}$ liter of carbon dioxide. In other words, the molecules of carbon dioxide so intermingle with the molecules of hydrogen that every part of each bottle is a perfect mixture containing 2 molecules of carbon dioxide to every 1 molecule of hydrogen. The intermingling of gaseous molecules, without the aid of outside agencies, is called gaseous diffusion. The mixture resulting from the diffusion of gases is a permanent one, for, unlike liquids, the gases do not separate into layers in accordance with their densities.

16. The Effect of Heat on the Volume of a Gas. During the latter part of the 18th and the early part of the 19th century, considerable work on the influence of temperature changes on the behavior of gases was done by different investigators, prominent among whom were Gay-Lussac and Charles, the latter being generally credited with the discovery that *the pressure remaining constant, a gas expands directly according to the increase in its temperature.* This is known as Charles' law, which may be interpreted to mean that, given a known volume of a gas at a certain temperature and pressure, the volume of this gas will increase a like amount for every degree rise in its temperature, provided the pressure upon it is kept constant. The extent to which a gas expands for each degree rise in temperature, is called the *coefficient of expansion* and is represented by the figure .003676, or approximately $\frac{1}{273}$. Thus, if a liter of oxygen at 0° C. and 760 millimeters pressure is heated to 1° C. and the pressure is readjusted to 760 millimeters, the volume will have increased $\frac{1}{273}$ and will occupy a space of $1\frac{1}{273}$ liters.

On the other hand, a gas will also contract $\frac{1}{273}$ of its volume for every degree decrease in its temperature, so that when a point 273° below zero is reached, the gas, according to Charles' law, would occupy no volume. This conception, however, would hardly agree with the theory regarding the conservation of matter, so in this case the space between the molecules of the gas must again be taken into account. Then, theoretically, upon cooling a gas, the intermolecular spaces are gradually decreased until at $-273°$ C. they no longer exist. Actually, however, the gas would liquefy before a temperature of $-273°$ C. were reached and Charles' law could not then be applied.

Facts such as these are easily verified by experiment and may be expressed by the formula

$$\frac{V}{V'}=\frac{T}{T'}$$

in which V = original volume;
V' = new volume;
T = original temperature;
T' = new temperature.

The temperatures represented by T and T' are measured on the absolute scale and are therefore equivalent to 273 plus the temperature on the centigrade scale. For instance, 10° on the centigrade scale is equivalent to 273+10, or 283° absolute, and, for the sake of clearness, the formula may be written:

$$\frac{V}{V'}=\frac{T+t}{T'+t'}$$

in which
V = original volume;
V' = new volume;
T = 273°;
T' = 273°;
t = original degrees centigrade;
t' = new degrees centigrade.

Several examples showing how the different values are substituted for the letters of the formula will make this phase of the subject more clear.

EXAMPLE 1.—If a quantity of oxygen amounting to 100 liters at 12° C. is cooled down to a temperature of 5° C., what will be the new volume occupied by the gas?

SOLUTION.—By substitutions in the formula,

$$\frac{100}{V'}=\frac{273+12}{273+5} \text{ or, } \frac{100}{V'}=\frac{285}{278}$$

Then, $285\,V'=278\times 100$

$$V'=\frac{278\times 100}{285}=97.54 \text{ liters, new volume.}$$

EXAMPLE 2.—A gas occupies a volume of 400 cubic centimeters at 35° C. What volume will it occupy when the temperature is lowered to −15° C.?

SOLUTION.—By substitution in the formula,

$$\frac{400}{V'}=\frac{273+35}{273-15} \text{ or, } \frac{400}{V'}=\frac{308}{258}$$

Then, $308\,V'=258\times 400$

$$V'=\frac{258\times 400}{308}=335.06 \text{ cubic centimeters, new volume. Ans.}$$

17. The Effect of Pressure on the Volumes of Gases. The effect of pressure on the volumes of gases was investigated by Robert Boyle, who, in the year 1661, found that if the temperature of a gas is kept constant, a given volume will

vary inversely as the pressure put upon it. In other words, the volume of a gas decreases as the pressure upon it increases and increases as the pressure is decreased. This discovery, which antedated the work of E. Mariotte about fourteen years, is called *Boyle's law* and may be expressed by the formula

$$\frac{V}{V'}=\frac{P'}{P}$$

in which V = original volume;
V' = new volume;
P' = new pressure;
P = original pressure.

That Boyle's law holds good for all practical purposes may easily be shown by a simple experiment. The apparatus shown in Fig. 3 consists of a glass **U** tube mounted on a wooden stand. The limb a of the tube is sealed and the upper end of limb b is open to the air. If a quantity of mercury is poured into the open end so as to fill the **U** completely and then, by tilting, if necessary, to allow some of the air to escape from the short limb, the levels of the mercury in each limb are made equal. The pressure on the mercury in the limb b will then be the same as that of the atmosphere and, therefore, the pressure on the confined air in the closed limb a will be 1 atmosphere. Now, if sufficient mercury is added so that a column in limb b of about 30 inches is obtained (see Art. 9), a pressure of 2 atmospheres will be exerted on the air in limb a and the volume of this air will be found to have decreased one-half. If it is remembered, then, that 29.922 inches, or 760 millimeters of mercury, is equivalent to a pressure of 1 atmosphere, and, with apparatus sufficiently large and strong, it can be shown that, given a certain volume of a gas, this volume can be made to decrease according to the increase in pressure. Thus, a volume of 1 liter is decreased to

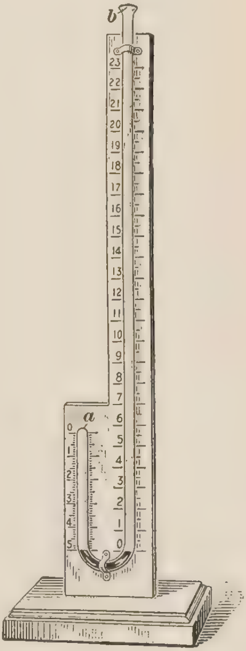


FIG. 3

$\frac{1}{2}$ liter by a pressure of 2 atmospheres; to $\frac{1}{3}$ liter by a pressure of 3 atmospheres, and so on.

The use of the formula expressing Boyle's law, in solving practical problems, is shown by the following examples:

EXAMPLE 1.—A gas occupies a volume of 100 liters at a pressure of 725 millimeters. What volume will it occupy at 760 millimeters?

SOLUTION.—The formula is, $\frac{V}{V'}=\frac{P'}{P}$

By substitution, $\frac{100}{V'}=\frac{760}{725}$

or $760\,V'=725\times100$

$$V'=\frac{725\times100}{760}=95.39 \text{ liters, new volume. Ans.}$$

EXAMPLE 2.—A gas occupies a volume of 10 cubic centimeters at 780 millimeters. What will be the volume if the pressure is decreased to 750 millimeters?

SOLUTION.—By substitution, $\frac{10}{V'}=\frac{750}{780}$

or $750\,V'=780\times10$

$$V'=\frac{780\times10}{750}$$

$V'=10.4$ c. c., the new volume. Ans.

18. The Combined Effects of Temperature and Pressure Changes on the Volume of a Gas.—The laws of Boyle and Charles, combined, may be stated as follows: The volume of a gas varies directly as the temperature and inversely as the pressure. The combination may also be expressed by the formula,

$$V'=\frac{V\,P\,T'}{P'\,T}$$

which may be derived as follows:

Charles' law: $\frac{V}{V'}=\frac{T}{T'}$

Boyle's law: $\frac{V}{V'}=\frac{P'}{P}$

Then, $\frac{V}{V'}=\frac{P'\,T}{P\,T'}$

and $$V'P'T = VPT'$$

$$V' = \frac{VPT'}{P'T}$$

in which
V' = new volume;
V = original volume;
P' = new pressure;
P = original pressure;
T' = new temperature;
T = original temperature.

It must be remembered that temperatures are measured on the absolute scale and that both T' and T represent 273 + degrees centigrade. The following example illustrates the application of the formula:

EXAMPLE.—A gas occupies a volume of 250 liters at a pressure of 745 millimeters and a temperature of $-15°$ C. What volume will it occupy if the pressure is increased to 765 millimeters and temperature to 20° C.?

SOLUTION.— $$V' = \frac{VPT'}{P'T}$$

By substitution, $$V' = \frac{250 \times 745 \times (273+20)}{765 \times (273-15)}$$

Then, $V' = 276.4$ liters, new volume. Ans.

In a subsequent Section, under Chemical Calculations, the student will have occasion to solve problems involving the principles set forth by the laws of Boyle and Charles. He is, therefore, urged to examine carefully the methods given for the solution of problems dealing with gaseous volumes.

VOLUME RELATIONS OF GASEOUS MOLECULES

COMBINATION BY VOLUME

19. Laws of Gay-Lussac and Avogadro's Hypothesis. As the result of his investigations, Gay-Lussac concluded (1808) that:

1. *The ratio in which gases combine by volume is always a simple one.*

2. *The volume of the resulting gaseous product bears a simple ratio to the volumes of its constituents.*

A few years later (1811) Avogadro formulated his hypothesis which states that *equal volumes of all gases at the same temperature and pressure contain the same number of molecules.* Therefore, according to this hypothesis, if we assume that in a given volume of a gas the number of molecules can in some manner be decreased, the volume of the gas must also be necessarily decreased. If we again assume that in a given volume of any gas each molecule is diatomic, and that by some means the molecule can be made tetratomic—the number of atoms remaining the same—the number of molecules will be reduced one-half, since each molecule contains twice the number of atoms; and this reduction of molecules is naturally accompanied by a corresponding decrease of the volume; that is, the volume of the gas will also be reduced one-half.

Or, if we assume that the diatomic molecule could be made triatomic, the number of molecules and consequently the volume, would be reduced one-third.

To apply this reasoning to the facts of volume combination, we will consider separately the combination of hydrogen with *monads*, *dyads*, and *triads*, assuming all their molecules to be diatomic.

1. *Combination of a Monad With Hydrogen.*—Each atom of a monad combines with an atom of hydrogen; before they combine, their molecules are each diatomic, and each molecule of the compound is also diatomic; if there was 1 volume of each before the combination, the number of compound molecules after the combination takes place is exactly equal to the sum of the molecules of the monad and hydrogen before they combined, and the result is 2 volumes of the compound.

Monads, then, combine with one another, volume to volume, yielding 2 volumes of the product.

ILLUSTRATION 1.—The monad atom chlorine, *Cl*, and the monad atom hydrogen, *H*, combine to form hydrochloric acid, *HCl*. Their molecules being diatomic, they unite, molecule to molecule, volume to volume, and, consequently, the number of molecules and the volume they occupy will

remain exactly the same after combination has taken place as it was previous to it. This may be represented diagrammatically; thus:

$$\boxed{H_2} \quad \text{and} \quad \boxed{Cl_2} \quad \text{form} \quad \boxed{2HCl}$$

2. *Combination of a Dyad With Hydrogen.*—A dyad atom will require 2 atoms of hydrogen; 1 molecule will require 2 molecules of hydrogen; and 1 volume, 2 volumes of hydrogen; or, to express this fact in other words, dyads combine with monads in the ration of 1 to 2.

As the resulting molecule is triatomic, it is evident that 3 diatomic molecules have combined to form 2 triatomic molecules, and that the decrease in the number of molecules also causes a corresponding decrease in volume. Thus 3 volumes of simple gas give 2 volumes of compound gas, a condensation of 3 volumes to 2 volumes taking place during combination.

Dyads, then, combine with monads in the ratio of 1 to 2, and yield 2 volumes of the product.

ILLUSTRATION 2.—An atom of oxygen is bivalent and its molecule diatomic. One atom of oxygen requires 2 atoms of hydrogen to form a molecule of steam, and 1 molecule of oxygen requires 2 molecules of hydrogen, and 1 volume requires 2 volumes. Thus:

$$\boxed{H_2} + \boxed{H_2} + \boxed{O_2} = \boxed{2H_2O}$$

3. *Combination of a Triad With Hydrogen.*—One triad atom requires 3 monad atoms for saturation, 1 molecule requires 3 molecules, and 1 volume requires 3 volumes; since the new molecule is tetratomic, the number of molecules and the corresponding volume they occupy must be reduced one-half.

Triads then unite with monads in the ration of 1 to 3, yielding 2 volumes of the product.

ILLUSTRATION 3.—The trivalent atom of nitrogen, N, requires 3 atoms of hydrogen to form 1 molecule of ammonia, or

$$\boxed{H_2} + \boxed{H_2} + \boxed{H_2} + \boxed{N_2} = \boxed{2NH_3}$$

As 4 diatomic molecules yield 2 tetratomic molecules, 1 volume of nitrogen and 3 volumes of hydrogen will yield 2 volumes of ammonia gas.

LIQUEFACTION OF GASES

20. Process.—As reference is occasionally made to liquefied gases, a brief explanation will be made of the process by which liquefaction of gases is produced.

Under atmospheric pressure, a great many substances may be either gaseous, liquid, or solid, depending on the prevailing temperature. For instance, water is liquid below a temperature of 100° C. and is gaseous above it; alcohol is liquid below 78° C. and is a vapor above it; sulphur dioxide boils at −8° C., and, if it were impossible to reduce the temperature below 0° C., would only be known as a gas.

21. When the temperature of a gas is sufficiently reduced and the gas is subjected to a high pressure, there is a tendency for it to liquefy. Faraday was among the first of the early experimenters to liquefy ammonia, chlorine, and carbon dioxide by cooling and compressing the gases simultaneously. The apparatus employed by him was very simple, consisting merely of a piece of thick-walled glass tubing, bent and sealed as shown in Fig. 4. The materials necessary for the formation of the gas were placed in the tube, which was then sealed. The limb *d* was immersed in a freezing mixture, such as ice and sodium chloride, or ice and calcium chloride, depending upon the temperature desired, while the limb *c* was heated. If, for instance, the limb *c* contained sodium carbonate, the carbon dioxide liberated upon heating was condensed to a liquid in *d*. The diagrammatic sketch, Fig. 5, illustrates the principles involved and the general method of procedure followed in the liquefaction of gases.

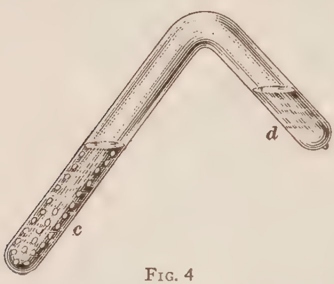


FIG. 4

22. The pump *a*, Fig. 5, draws air or gas through the branch pipe *m* into the apparatus. When a sufficient quantity has been obtained this branch is closed by means of the valve shown at the junction of the pipes. The pump, which is able

to exert a pressure of about 50 atmospheres, or about 735 pounds per square inch, forces the gas into the tube *c* in the direction of the arrows and it escapes, eventually, through the orifice *d* into the receiver *h*.

The heat developed by the compression of the gas in the pump is removed from the gas while passing through the tube *c*, the first portion of this tube being cooled by the water-jacket *f*. The temperature of the gas is also lowered as a result of its expansion on leaving, the orifice *d*, and a further reduction of temperature takes place as the gas expands on entering the large tank *l*. The cooled gas serves now as a means for cooling the gas descending through the tube *g*, which gas is again cooled by reason of its expansion into *h*. As the gas is continually passing through the apparatus its temperature is gradually reduced, until finally the critical temperature is reached and the gas condenses. The liquid gas may be drawn off through the tube *e*.

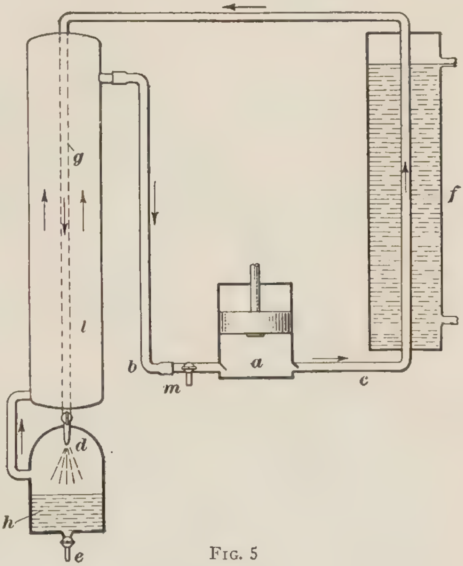


FIG. 5

23. By the term critical temperature is meant the temperature below which a gas will condense and become liquid, and above which temperature no amount of pressure will cause it to liquefy.

The pressure which is just sufficient to cause a gas to liquefy at the critical temperature, is known as the *critical pressure*. At temperatures below the critical temperature, the pressure necessary to liquefy a gas is less than the critical pressure.

SOLUTIONS AND THEIR IONIZATION

SOLUTIONS

CLASSIFICATION

24. Emulsions, Colloidal Suspensions, and Solutions.—A substance mixed with a liquid may result in a suspension of the substance, in a finely divided state, throughout the liquid or in the disappearance of the substance into the liquid with the formation of a clear, transparent, homogeneous mixture which does not separate into its constituents, no matter how long it may be allowed to stand. The latter mixture is a true solution; the substance dissolved is the solute, and the dissolving liquid, the solvent.

If the substance is a liquid that is suspended throughout the liquid in little drops, the mixture is called an emulsion. Butter fat and some other constituents form milk, which is an emulsion.

If the substance is a solid suspended in so finely divided a condition throughout the liquid that the mixture is not made noticeably cloudy and the solid does not settle out even after long standing and yet does not form a true solution, a colloidal suspension or colloidal solution is formed and the solid forming it is called a colloid. Starch, glues, and gums are typical colloids.

Colloidal suspensions and emulsions should not be confused with true solutions. In time, constituents in an emulsion separate from each other. Colloidal suspensions differ from solutions in that rays of light passing through colloidal suspensions become visible, similar to a sunbeam in a dark, dusty room, but when passing through a true solution they are invisible.

VARIATIONS IN SOLUBILITY

25. Solubility of Substances.—The thought naturally arises as to whether there is any limit to the quantity of a substance that may be dissolved in a given quantity of solvent. Some liquids can be dissolved in other liquids in unlimited proportions, as, for example, alcohol in water. Potassium chlorate, $KClO_3$, will form a solution when added to 100 cubic centimeters of water at 18° C., until 6.6 grams of it have been introduced but no quantity beyond this amount will dissolve in this amount of water. In fact, most solids may be dissolved in a liquid only up to a certain limit, which varies from scarcely perceptible quantities up to large amounts.

A solution in which a solvent will dissolve no more of the solute under existing conditions even when in contact with some of the undissolved substance used as the solute, is called a saturated solution. The ratio of the weight of a solute to the weight of a solvent, saturated by the solute at a given temperature, is known as the solubility of the solute.

26. Table V shows the solubility of several common substances in 100 cubic centimeters of water at 18° C. The table is divided into a number of vertical and horizontal rows. On top of the vertical rows are placed a given number of elements representing the positive radicals of the substances, and at the left of the horizontal rows are placed a number of groups of elements indicating the negative radicals. The number in the square at which two rows intersect, shows the number of grams of the various substances soluble in 100 cubic centimeters of water at 18° C. For instance, the square at which the rows headed K and Cl intersect contains the number 32.95, which represents the number of grams of potassium chloride, KCl, soluble in 100 cubic centimeters of water at 18° C. Again, the rows headed Mg and SO_4 intersect at the number 35.43. The combination of the symbols Mg and SO_4 represents magnesium sulphate, $MgSO_4$, and the number 35.43 indicates the number of the grams of this compound soluble in 100 cubic centimeters of water at 18° C.

TABLE V

WEIGHT, IN GRAMS, OF SUBSTANCES SOLUBLE IN 100 C. C. OF WATER AT 18° C.

	K	*Na*	*Li*	*Ag*	*Tl*	*Ba*	*Sr*	*Ca*	*Mg*	*Zn*	*Pb*
Cl	32.95	35.86	77.79	.00013	.3	37.24	51.09	73.19	55.81	203.9	1.49
Br	65.86	88.76	168.7	.00001	.042	103.6	96.52	143.3	103.1	478.2	.598
I	137.5	177.9	161.5	.00000035	.006	201.4	169.2	200.0	148.2	419.0	.08
F	92.56	4.44	.27	195.4	72.05	.16	.012	.0016	.0087	.005	.06
NO_3	30.34	83.97	71.43	213.4	8.91	8.74	66.27	121.8	74.31	117.8	51.66
ClO_3	6.6	97.16	313.4	12.25	3.69	35.42	174.9	179.3	126.4	183.9	150.6
BrO_3	6.38	36.67	152.5	.59	.30	.8	30.0	85.17	42.86	58.43	1.3
IO_3	7.62	8.33	80.43	.004	.059	.05	.25	.25	6.87	.83	.002
OH	142.9	116.4	12.04	.01	40.04	3.7	.77	.17	.001	.0005	.01
SO_4	11.11	16.83	35.64	.55	4.74	.00023	.011	.20	35.43	53.12	.0041
CrO_4	63.1	61.21	111.6	.0025	.006	.00035	.12	.4	73.0		.00002
C_2O_4*	30.27	3.34	7.22	.0035	1.48	.0085	.0046	.00055	.03	.00064	.00016
CO_3	108.0	19.39	1.3	.003	4.95	.0023	.0011	.0013	.1	.004	.0001

* Oxalates

EFFECT OF TEMPERATURE ON SOLUBILITY

27. Solubility of Solids and Gases as Affected by Temperature.—Temperature has an important bearing on the solvent action of liquids, usually increasing it as the temperature rises, when the solute is a solid; and decreasing it as the temperature rises, when the solute is a gas. Table VI

TABLE VI

SOLUBILITY OF GASES IN WATER

Name of Substance	By Volume			By Weight		
	0° C.	15° C.	100° C.	0° C.	15° C.	100° C.
Acetylene......	1.73	1.15		.20	.13	
Air...........	.02881	.02045	.01105	.02936	.02090	
Ammonia......	1298.9	802.4		98.7	60.6	
Carbon dioxide.	1.713	1.019		.3347	.1971	
Carbon monoxide.........	.03537	.02543	.0141	.0044	.0031	
Chlorine.......	4.61	2.635		1.46	.8493	
Hydrogen chloride.........	506.5	461.5		82.5	75.2	
Hydrogen.....	.0203	.0183	.1066	.00018	.00016	
Hydrogen sulphide.......	4.686	3.056		.710	.458	
Methane	.05563	.03690	.0170	.00396	.00260	
Nitrogen......	.02388	.01786	.01	.00298	.00221	
Oxygen........	.0489	.03415	.017	.00695	.0048	
Sulphur dioxide.	79.789	47.276		22.83	13.54	

shows the solubility of some gases in water at 0° C., 15° C., and 100° C.

The term *by volume* employed in Table VI means the volume of the gases, at a temperature of 0° C. and a pressure of 760 millimeters, that may be dissolved by 1 volume of water. The term *by weight* means the number of grams of gas dissolved by 100 grams of water. For example, the table shows that .0489 volume of oxygen is dissolved in 1 volume of water at 0° C. to form a saturated solution, and that .00695 gram of

oxygen is dissolved in 100 grams of water at 0° C. to form a saturated solution.

28. Supersaturated Solutions.—If a solution saturated at a high temperature is allowed to cool, less solute can be held in solution and the excess will usually deposit from the solution, maintaining saturation at the various temperatures. Sometimes the solute fails to crystallize out as the temperature falls, particularly when the solution is not disturbed in any way. Under this condition, the solution contains more of the solute than is ordinarily present in a saturated solution under existing conditions; it is then called a supersaturated solution. If a crystal of the dissolved substance is brought into contact with a supersaturated solution, the excess of solute immediately separates from the solution.

29. Strengths of Solution.—The term strength, used in many ways in chemistry, is not sufficiently definite to be used for expressing the proportions of solvent and solute in solutions, and some other means of stating these proportions is needed.

The relative amounts of solvent and solute in a solution is generally described as the *concentration* of that solution. A dilute solution is a solution containing a small proportion of solute, and a concentrated, or strong, solution is a solution containing a large proportion of solute. The removal of part of the solvent is called concentrating and the removal of all the solvent by evaporation is described as evaporating to dryness.

It should be borne in mind that a saturated solution is not necessarily a concentrated solution for, in many cases, but small amounts of substances may be needed to produce saturated solutions. Therefore, the terms pertaining to concentration are not used in connection with those applying to degree of saturation.

IONIZATION

30. Conductors.—The disappearance of solutes in solvents to form homogeneous, clear, transparent mixtures is a phenomenon that can readily be observed, but what actually takes place within the solution needs further consideration.

The effects of an electric current serve to bring out several facts of importance to the study of changes during solution. Electric currents may be conveyed from one location to another by electric conductors in which there is no evident simultaneous movement of the matter of which the conductor consists. For example, a copper wire may conduct an electric current without any evident movement of its constituent particles of copper. Such conductors are known as conductors of the first class. Then there are conductors of electric currents in which there is a simultaneous movement of the particles of the conductors. Solutions of acid, bases, and salts are examples of this type of conductors, known as conductors of the second class. A further study of the nature of solutions at this point is concerned chiefly with the conductors of the second class.

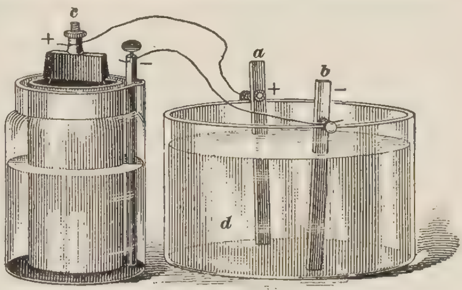


Fig. 6

31. Electrolysis.—Absolutely pure sulphuric acid, H_2SO_4, does not conduct an electric current, but if a solution of it is formed with water, it conducts a current readily. Solutions that conduct an electric current are called electrolytes, though the term is often applied to the dissolved substance. For instance, though the term electrolyte applies to the solution of sulphuric acid in this particular instance, it is sometimes used to designate pure sulphuric acid also. in which case the thought is conveyed that a solution of sulphuric acid is an electrolyte.

The general method used in the electrolysis, or electrical decomposition, of a solution is illustrated in Fig. 6. Two plates or rods, *a* and *b*, made of suitable materials (metals or carbon) are connected to the source of an electric current, such as an electric generator or, as in this case, an electric cell *c*, and dipped into the electrolyte *d*. These plates or rods are called electrodes. The electrode *b* connected with the negative pole of the battery is the negative electrode, or cathode, while the electrode *a* connected with the positive pole is the positive electrode, or anode.

32. Sulphuric acid consists of a positive radical, H_2, and a negative, or acid, radical, SO_4. As two electric charges of opposite polarities attract each other, it follows that when an electric current is passed through a solution of sulphuric acid, the positive radical, H_2, passes toward and collects at the negative electrode, or cathode, *b* and the negative, acid radical, SO_4, passes toward the positive electrode, or anode, *a*. Particles of matter, such as the positive radical, H_2, or the negative radical, SO_4, that travel with the current are called ions. The ions that travel toward the cathode, as, for example, H_2, are called cations, and ions that travel toward the anode, as, for example, SO_4, are called anions. The hydrogen formed can be collected at the cathode; the SO_4 radical, on the other hand, reacts with the water, H_2O, present to form oxygen thus:

$$2SO_4+2H_2O=2H_2SO_4+O_2$$

The oxygen formed gathers at the anode and can be collected, and the sulphuric acid formed again breaks up into ions to repeat the changes described. The chemical change that takes place when an electric current is passed through an electrolyte is called electrolysis. The foregoing changes in the electrolysis of a solution of sulphuric acid are the changes that take place when water is decomposed by an electric current into its components, hydrogen and oxygen.

33. Theory of Ionization.—The Swedish chemist Arrhenius first advanced a theory on solutions known as the theory of ionization or dissociation. Today, it forms an impor-

tant part of chemical knowledge. The theory may be summarized in the following laws:

1. *The molecules of many substances, when dissolved in water, fall apart, or dissociate, into two or more parts called ions.*

2. *An ion differs from an atom or molecule in that it carries an electric charge.*

3. *Two kinds of ions are formed: one charged with positive electricity and the other with negative electricity, the sum of the positive charges being sufficient to neutralize exactly all the negative charges.*

4. *Only electrolytes dissociate into ions.*

34. The meaning of these laws may be brought out more clearly by considering the formation of a solution of common salt, sodium chloride, in water. According to the theory of ionization, some of the molecules of sodium chloride, $NaCl$, dissociate when dissolved in water into ions of sodium and chlorine. If an electric current were to be passed through this solution, it would be found that the sodium ions, which are charged with positive electricity, would pass toward the negative electrode and that the chlorine ions, which are charged with negative electricity, would pass toward the positive electrode. The electric charge carried by an ion is represented by placing either a plus (+) or a minus (−) sign above the symbol representing the ion. For instance, the dissociation of sodium chloride is shown in this way:

$$NaCl = \overset{+}{Na} + \overset{-}{Cl}$$

One plus or minus sign is used for each valence. The breaking up of sulphuric acid into ions would likewise be represented as follows:

$$H_2SO_4 = \overset{++}{H_2} + \overset{--}{SO_4}$$

In this case, each radical is divalent and two plus and two minus signs are used.

As soon as the sodium ions come into contact with the negatively charged electrode, or cathode, they give up their positive

charge and become ordinary atoms of sodium, and thereupon they react immediately with the water present to form sodium hydroxide and hydrogen; thus:

$$2Na+2H_2O=2NaOH+H_2$$

In like manner, the ions of chlorine are attracted to the positively charged electrode, or anode, where the electric charge is given up and the ions become atoms of chlorine. These atoms either unite with other chlorine atoms to form molecules of chlorine or react with water to form hydrogen chloride and oxygen; thus:

$$2Cl_2+2H_2O=4HCl+O_2$$

It should be borne in mind that the electric current does not cause the formation of ions, but merely directs them toward the oppositely charged electrodes. Ions are formed when the solute is dissolved in the solvent. All these laws have been verified by tests and can be accepted as facts.

There are some substances, such as sugar, that do not ionize when dissolved and these solutions do not conduct an electric current.

35. Ionization of Acids.—When an acid is dissolved in water, it dissociates into hydrogen ions, which always serve as cations, and into ions of the remaining radical, which always serve as anions. Hydrochloric acid dissolves in water to form cations of hydrogen and anions of chlorine; thus:

$$HCl=\overset{+}{H}+\overset{-}{Cl}$$

Sulphuric acid dissolves in water to form cations of hydrogen and anions of the SO_4 radical; thus:

$$H_2SO_4=\overset{++}{H_2}+\overset{--}{SO_4}$$

Nitric acid dissolves in water to form cations of hydrogen and anions of the radical NO_3; thus:

$$HNO_3=\overset{+}{H}+\overset{-}{NO_3}$$

In like manner, other acids form cations of hydrogen. Hence, an **acid** may be defined as a substance that produces hydrogen ions, when dissolved in water.

36. Ionization and Bases.—Bases dissociate into two kinds of ions when dissolved in water, one of which is always the hydroxyl group, *OH*, serving as an anion.

Sodium hydroxide, when dissolved in water, dissociates thus:

$$NaOH = \overset{+}{Na} + \overset{-}{OH}$$

Potassium hydroxide, when dissolved in water, dissociates thus:

$$KOH = \overset{+}{K} + \overset{-}{OH}$$

Calcium hydroxide, when dissolved in water, dissociates thus:

$$Ca(OH)_2 = \overset{++}{Ca} + \overset{--}{(OH)_2}$$

In like manner, other bases produce hydroxyl ions when dissolved in water. Hence, a **base** may be defined as a substance that produces hydroxyl ions, when dissolved in water.

37. Ionization and Salts.—Bringing together an acid and a base in proper proportions results in the disappearance of the properties of each. The resulting solution usually tastes neither sour or bitter, but is, on the contrary, salty. It has no effect on litmus, or on other indicators.

A study of the change that takes place when an acid, such as hydrochloric, is combined with the proper proportion of the base sodium hydroxide, both being in solution, shows that water is always one of the products formed. Written on the basis of ions, the change is:

$$\overset{+}{Na}, \overset{-}{OH} + \overset{+}{H}, \overset{-}{Cl} = \overset{+}{Na}, \overset{-}{Cl} + H_2O$$

The reaction shows that water is formed, and, unlike sodium and chlorine, does not remain dissociated as hydrogen and hydroxyl ions while in solution. A study of reactions of this kind has shown that hydrogen and hydroxyl ions cannot exist together in solution to any extent, but combine to form molecules of water, H_2O.

The change that forms a neutral substance, when an acid reacts with a base in the proper proportions, is called **neutralization,** and in the light of the theory of ionization. may be defined as the union of the hydrogen ion of an acid with the

hydroxyl ion of a base to form water. In like manner, a salt is a substance formed by the union of the anion of an acid with the cation of a base. In the foregoing example, the cation sodium of the base sodium hydroxide unites with the anion chlorine of the hydrochloric acid to form the salt sodium chloride.

38. Extent of Ionization.—It has been found that only a small fraction of the molecules in a solution ionize, depending on conditions. For instance, a dilute solution will allow a greater ionization of molecules than a concentrated solution. In other words, the greater the proportion of water (or other solvent used to form an electrolyte) the greater will be the extent of ionization.

The extent of ionization depends also on the nature of the substance dissolved. For example, at equal concentration, most salts ionize to about the same extent. Bases and acids, however, vary greatly in the degree to which they ionize when dissolved, for some are freely ionized and others but slightly.

39. Source of Electric Charges.—The thought naturally arises as to where the electric charges carried by ions are obtained. According to the modern theory, an atom consists of a minute nucleus of positive electricity surrounded by particles of negative electricity, called electrons, each having a mass equal to about one-seventeen-hundredth of that of an atom of hydrogen.

In this combination, the valences of the various elements are closely allied. An ion of chlorine, Cl, consists of an atom of chlorine plus one electron and thus has an excess of one unit negative charge; an ion of sodium, Na, consists of an atom of sodium minus one electron of sodium, and thus has an excess of one unit positive charge. When the ion of sodium unites with the ion of chlorine, the resulting product, sodium chloride, is neutral, for the excess of one unit of positive electricity in the sodium ion is neutralized by the excess of one unit of negative electricity in the chlorine ion. Hence, the atoms themselves supply the electric charges carried by ions.

40. In like manner, divalent elements when changed to ions have an excess of either two units of a positive charge or

two units of a negative charge, and one ion of a divalent element or group or two ions of a monovalent element or group are needed to neutralize the excess of electric units present. In other words, the valence of an element or radical designates the proportionate number of units of the electric charge carried by an ion of that element or radical. For instance, the divalent elements like calcium and barium form ions $\overset{++}{Ca}$ and $\overset{++}{Ba}$ and the divalent radical SO_4 forms the ion $\overset{--}{SO_4}$.

As the study of ionization is in itself a broad and extensive field of study, only a brief description of the subject can be given here, as far as it is applied to the ordinary chemical processes with which the student of chemistry comes into contact.

PHYSICAL PROCESSES

APPARATUS AND METHODS

INTRODUCTION

41. Principal Types of Apparatus.—Good work can be done by a chemist only when he is thoroughly familiar with the names and uses of the various kinds of apparatus needed to perform experiments and to make tests. The different types of apparatus shown on Plates I, II, and III will be described in detail in connection with the many operations dealt with in different parts of the text. It is advisable, however, to learn to associate the appearance of each piece of apparatus illustrated with its name, for it is knowledge that will be helpful in practical laboratory work. For this purpose each illustration is provided with the name of the instrument, apparatus, tool, etc., that it is intended to represent.

It should be understood, however, that the apparatus illustrated represents but a small portion of that required by a commercial laboratory which is engaged in making all kinds of tests. In most lines of commercial laboratory work, apparatus designed especially for certain kinds of work is often used.

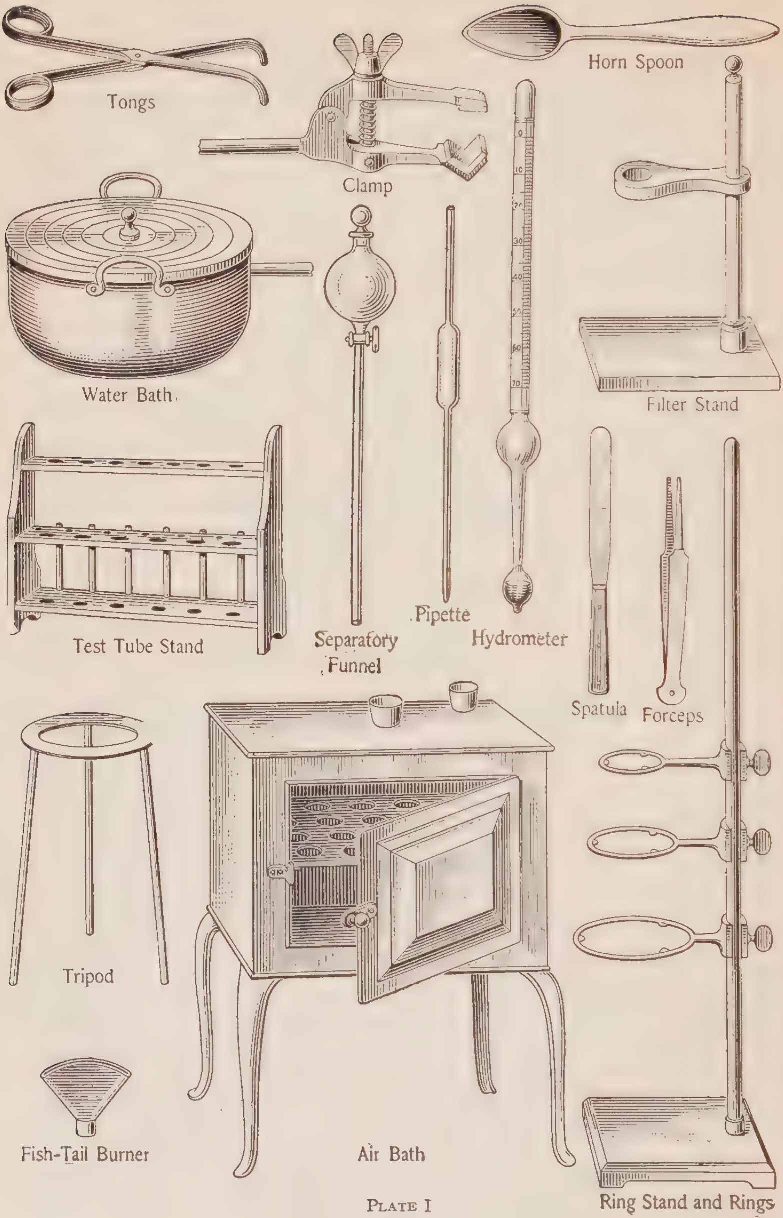

Tongs
Clamp
Horn Spoon
Water Bath
Filter Stand
Test Tube Stand
Separatory Funnel
Pipette
Hydrometer
Spatula
Forceps
Tripod
Fish-Tail Burner
Air Bath
Ring Stand and Rings

PLATE I

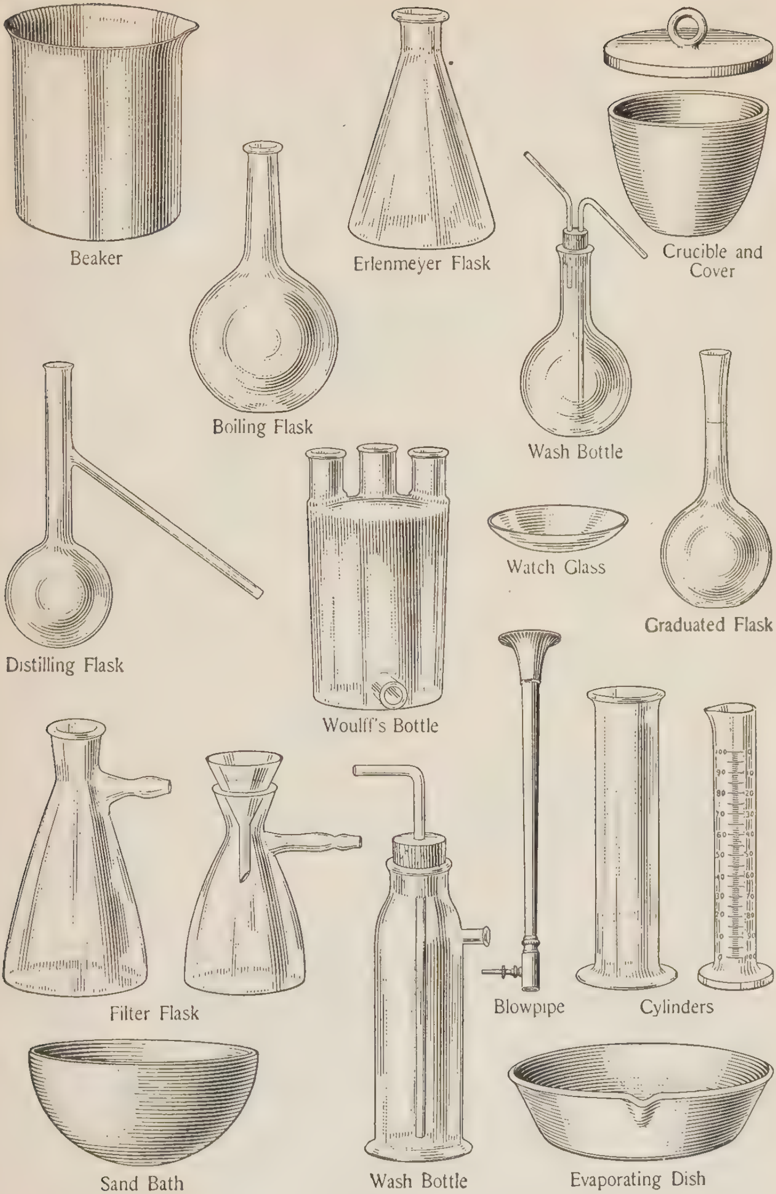

Beaker
Erlenmeyer Flask
Crucible and Cover
Boiling Flask
Wash Bottle
Distilling Flask
Woulff's Bottle
Watch Glass
Graduated Flask
Filter Flask
Blowpipe
Cylinders
Sand Bath
Wash Bottle
Evaporating Dish

PLATE II

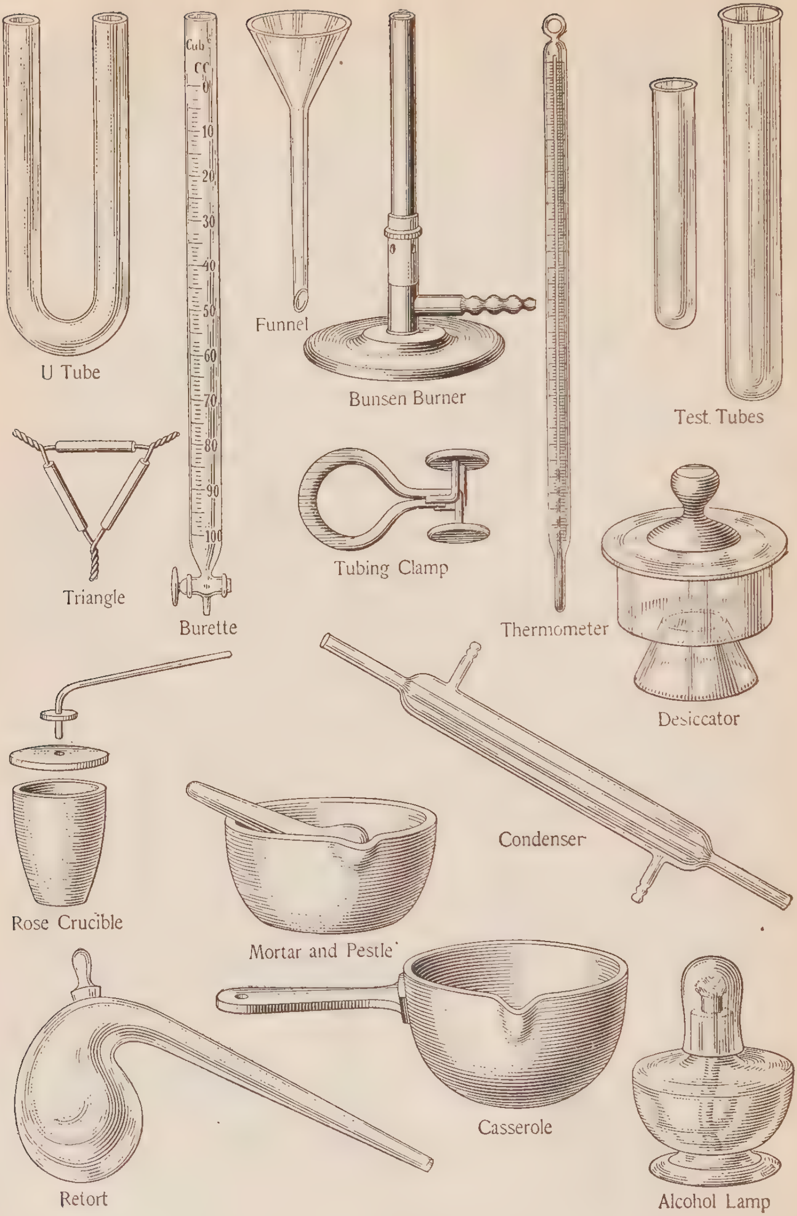

U Tube
Cub
CC
0
10
20
30
40
50
60
70
80
90
100
Funnel
Bunsen Burner
Test Tubes
Triangle
Burette
Tubing Clamp
Thermometer
Desiccator
Condenser
Rose Crucible
Mortar and Pestle
Retort
Casserole
Alcohol Lamp

Plate III

METHODS OF SEPARATION

42. Classification of Methods.—There are some operations in laboratory work that are constantly applied, particularly in the separation of substances from one another. These methods are of such general use that it is well for the student of chemistry to know what details must be observed and what points must be noted in them. In each case, advantage is taken of the fact that a constituent to be separated from a mixture has some property not possessed by the rest of the constituents.

The principal methods of separation are: Solution, decantation, filtration, crystallization, evaporation, distillation, sublimation, and ignition. The details to be observed in each of these processes should be studied carefully, for they find constant application in chemical work and are indispensable in laboratory operations. Only the details of operation are treated of in this part of the text, the principles upon which they are based being explained in another Section.

43. Solution, Decantation, and Evaporation.—If common table salt is placed in water it soon disappears and leaves a clear liquid mixture. The salt is said to have dissolved in the solvent, water, to form a solution of salt in water. Increasing the surface area of a substance by powdering it and heating the solvent after adding the substance to it, hastens the solution. A mortar and pestle are generally used to powder substances.

The fact that a substance is soluble enables it under certain circumstances to be separated from other substances. Suppose, for example, that a mixture of sand and salt is to be separated into its constituents. It has been determined that sand is insoluble (cannot be dissolved) in water and that salt is soluble (can be dissolved): facts that enable one to separate the substances completely.

The mixture is shaken up with water, a process that dissolves the salt and leaves the sand unaffected. The sand is allowed to settle to the bottom and the clear solution on top, called the *supernatant liquid*, is carefully poured off into a basin without

disturbing the settled sand. The operation of pouring off a supernatant liquid without disturbing the sediment is called *decantation*. Washing by decantation is accomplished by pouring off the supernatant liquid, adding fresh water, mixing thoroughly, allowing the insoluble substance to settle, and again pouring off the supernatant liquid.

If heat is applied to the vessel containing the salt solution, water passes off as steam and crystals of salt form in the basin. The conversion of a liquid to a vapor is called *evaporation*, a process that is used extensively in chemical operations.

Either a test tube or a beaker can be used as the vessel in which salt, water, and sand are mixed; an evaporating dish serves as the vessel in which to collect the salt solution and from which to evaporate the water. Heat can be applied by means of either a Bunsen burner or an alcohol lamp; a piece of wire gauze is generally placed on a tripod, and the basin containing the salt solution is placed on the gauze.

44. Filtration.—Unlike the sand mentioned in the foregoing article, there are some solids so finely divided that they float in a liquid and settle only with difficulty, in which case the process of decantation cannot be used. **Filtration**, the operation that must be used in this instance to separate the soluble substance from the insoluble, is the process of separating a liquid from an insoluble substance by pouring the mixture onto a porous material, in which case the liquid passes through the pores and the insoluble substance remains on the porous material.

For illustration, suppose that a mixture consisting of powdered chalk and salt is to be separated into its constituents. The mixture is thoroughly shaken with water to dissolve the salt and is then poured onto a folded filter paper, arranged in a glass funnel. The solution of salt will pass through the paper and the chalk will remain on the paper. The liquid that passes through the porous material during filtration is called the *filtrate*. Asbestos, talc, and cotton are porous materials often used for filtering purposes. In every case, one should wet a filter paper after it has been placed in a funnel and before any of the material to be filtered is introduced.

45. Fig. 7 shows how a filter paper is folded for use in a funnel. A piece of soft porous paper, as shown at *1* (blotting paper 3 inches in diameter will do for ordinary practice), is doubled twice and then opened into a cone, taking three folds of the paper on the one side and one on the other, as shown at *2* and *3*, respectively. The cone of paper is placed in a glass funnel and moistened with water. Care should be taken that the point of the folded filter is not broken.

As filtration is one of the most important of all processes used in the laboratory, one should observe carefully every detail upon which the operation depends. As an illustration, let it be supposed that a solution of sodium carbonate is added to a

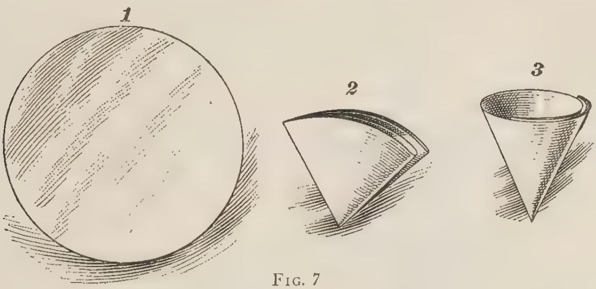


FIG. 7

solution of barium chloride. A white insoluble substance is formed, as a result of the chemical reaction which takes place,

$$Na_2CO_3+BaCl_2=2NaCl+BaCO_3$$

This insoluble substance, barium carbonate, $BaCO_3$, is called a *precipitate*, which is defined as an insoluble substance formed from a solution. Precipitation, or the process of forming a precipitate, is brought about, as a general rule, by the formation of an insoluble substance, as a result of a chemical action between two soluble substances in solution.

Let it be supposed that the precipitate formed when the solution of sodium carbonate is added to the solution of barium chloride, is to be separated from the rest of the mixture. The solution and precipitate are poured onto the filter by holding a glass rod or thin piece of glass tubing against the lip of the beaker or test tube, and by tipping the vessel containing the mixture, as shown in Fig. 8. The clear liquid, or filtrate,

passes through the pores of the paper and is collected in a suitable vessel such as a beaker, the precipitate remaining on the paper. Some clean water is poured on the paper and the precipitate in order to wash them free from any soluble substances that have not yet passed through the paper.

Care should be taken when pouring the mixture onto the filter to hold the glass rod or thin glass tubing close to the filter paper in order to guard against spattering or the liquid running down on the outside of the vessel. A wash bottle is generally used, as shown in Fig. 9, to supply the water needed to wash the soluble substances through the paper. The wash bottle is also used, as shown in Fig. 10, to remove the last portion of the mixture from the vessel containing it.

Fig. 8

46. Crystallization. A mixture may contain two soluble substances that differ from each other in their degree of solubility. In cases such as this, the mixture is completely dissolved by boiling. As the solution cools, the less soluble substances will separate out in a definite shape and the more soluble substances will remain in solution. The process in which a soluble substance separates from a solution, as a definitely shaped body, is called *crystallization*, and the definitely shaped body is called a *crystal*.

For example, a mixture of equal parts of potassium chlorate and potassium chloride is placed in a test tube and just enough water is added to dissolve the substances upon boiling. On allowing the solution to cool, crystals of the less soluble potas-

sium chlorate will separate from the solution. These crystals may be removed from the solution by filtration, then purified

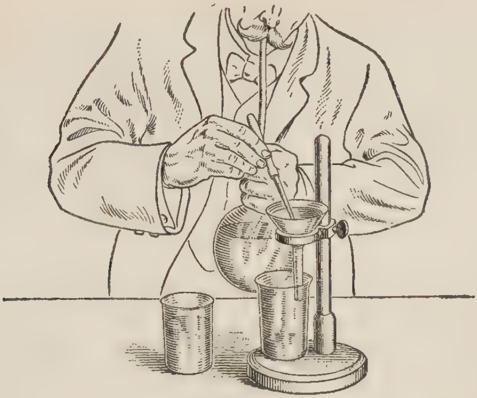


Fig. 9

by washing with a small amount of cold water, and then dried at a very low temperature.

47. Fractional Crystallization.—If equal parts of sodium and potassium nitrates are dissolved in hot water, and the solution then slowly cooled, potassium nitrate will crystallize first and then the sodium nitrate. Each lot of crystals may be

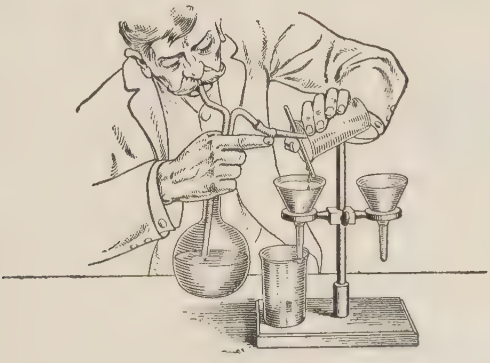


Fig. 10

redissolved and the process of cooling and crystallization repeated, each repetition of the process resulting in the further

purification of the two salts. This is called *fractional crystallization.*

48. Distillation.—In the case of a mixture of a liquid and a solid or a mixture of two or more liquids, it is sometimes necessary to separate the component parts of the mixture into the original constituents; in this case the process of distillation is used. **Distillation** is a process, in which a substance is first liquefied, if it is a solid, by means of heat, or if already a

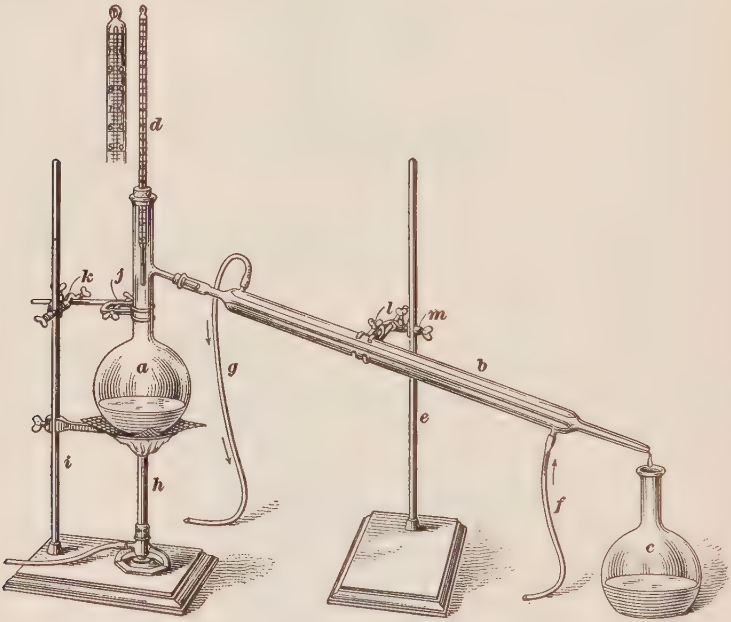


FIG. 11

liquid, it is evaporated, or volatilized, by the application of heat to the containing vessel, the volatile matter, or vapor, then being passed through a condenser and again liquefied or condensed.

For example, if it is desired to separate a mixture containing colored matter and water (a water-ink mixture will answer), the work may be done as follows: The mixture is placed in the round-bottomed distillation flask a, Fig. 11, which is connected

to the condenser *b* and which also contains the thermometer *d*. Heat is applied to the flask by means of the modified Bunsen burner *h*, the flask being supported by means of an iron ring covered with a piece of wire gauze and clamped to the ring stand *i*. The flask is held in its vertical position by means of the universal clamp *j* and the clamp holder *k*. When the liquid in the flask begins to boil or distil, the vapors pass through the side tube of the flask into the condenser, which is supported by the ring stand *e*, the universal clamp *l*, and the clamp holder *m*. This condenser is kept cold by the water entering the water jacket, not the tube itself, at *f* and leaving at *g*. When the vapors strike the cold inner tube of the condenser, they liquefy or condense and are collected in the flat-bottomed Florence flask *c*, which in this case acts as the receiver. The condensed liquid, termed the condensate or distillate, is the water of the original mixture. It will be found to be perfectly clear, the coloring matter of the ink being left behind as a residue in the distilling flask.

49. Fractional Distillation.—This operation may be illustrated as follows: Suppose there is a solution of benzene and xylene, two organic coal-tar products, and that it is required to separate them as completely as possible by means of distillation. The boiling point of benzene is 80° C. while that of xylene is about 142° C. Taking 100 cubic centimeters of a mixture, containing 50 cubic centimeters of each, and distilling it, the greater part of the benzene will come over first while as the distillation proceeds, the distillate will become richer and richer in xylene. Then, if in the first distillation two portions, or fractions, of 50 cubic centimeters each, had been collected, the first would have contained most of the benzene and the second most of the xylene. If these fractions are again separately distilled and other fractions collected at 10° C. below and above the boiling points of benzene, in the one case, and of xylene, in the other, it will be seen that if this procedure is continued for a sufficient number of distillations, two fractions will ultimately be obtained, which will consist of nearly pure benzene and xylene. Of course, results as good as these

can hardly be obtained with the ordinary laboratory apparatus, but they may be obtained by employing specially designed distilling apparatus.

50. Distillation Under Diminished Pressure. Throughout the subject of chemistry expressions such as the following are often met with: *distillation under diminished pressure*, *distillation in vacuo*, and as it is important that the meaning of these expressions should be understood, they will be explained by means of Fig. 12.

In Fig. 12 is shown a manometer of the form commonly used in laboratories when making distillations at pressures less than that of the atmosphere. At sea level the average pressure exerted by the atmosphere is equal to 14.7 pounds per square inch, and this pressure corresponds with that required to support a column of mercury, 760 millimeters in height, in a vertical, exhausted tube.

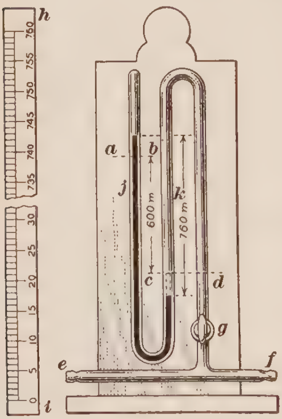


FIG. 12

51. The apparatus, illustrated by Fig. 12, consists of a bent glass tube, sealed at the upper end and fitted with a stop-cock g at the other end; this end is joined to a short tube $e\,f$. If the ends e, f and the stop-cock g are left open, the pressure exerted upon the lower end of the mercury column is that of the atmosphere. If now a vacuum pump is attached to the end f, after the end e has been closed, the distance between the two ends, or levels, of the mercury column, which is normally equal to 760 millimeters, will gradually decrease and the ends may shortly occupy the positions indicated by the lines $a\,b$ and $c\,d$. This position may, for instance, correspond to a pressure of 600 millimeters.

Continuing the operation of the vacuum pump, the levels of the mercury columns in the two limbs j and k tend to approach each other as zero pressure is reached.

In commercial instruments, a scale graduated in millimeters, similar to that shown at $h\ i$, is employed. This scale may be adjusted so that its zero point is on the same level as that of the lower end of the mercury column, thus allowing the distance between the levels of the mercury in each limb of the manometer to be read off directly on the scale.

52. When a distillation under diminished pressure is to be made, the apparatus may be set up as shown in Fig. 13. One of the open ends of the manometer is connected to some type of vacuum pump, while the other is connected to the side-tube of an ordinary filter flask, which acts as a receiver. These connections are made by means of heavy, thick-walled rubber tubing, commonly called pressure tubing. For the sake of convenience, an adapter n is used between the lower end of the condenser and the top of the filter flask.

In low-pressure work, it is very necessary that all joints be tight or it will be impossible, in most cases to obtain the decrease in pressure desired and, for this reason, all of the stoppers used as shown in Fig. 13 are made of rubber. However, if rubber is attacked by the substance being distilled, cork stoppers which have been coated with collodion may be used. Collodion is a solution of nitrocellulose, the solvent usually being a mixture of ether and alcohol (see *Organic Chemistry*).

Having set up the apparatus as shown and with the substance to be distilled in flask a, to begin the distillation it is merely necessary to light burner h, start the water going through the condenser, and then start the vacuum pump.

Distillations under diminished pressure are usually resorted to when organic compounds are to be distilled and which decompose when heated to their boiling points at atmospheric pressure. Glycerine, for example, boils at 290° C., but it rapidly decomposes at this temperature; therefore, in order to obtain the practically pure colorless product, it must be distilled under diminished pressure whereby the boiling point is reduced.

53. Sublimation.—Most solids, as, for example, ice, will first form a liquid and then a vapor when heated. There are a few solids, however, such as iodine, ammonium chloride, cam-

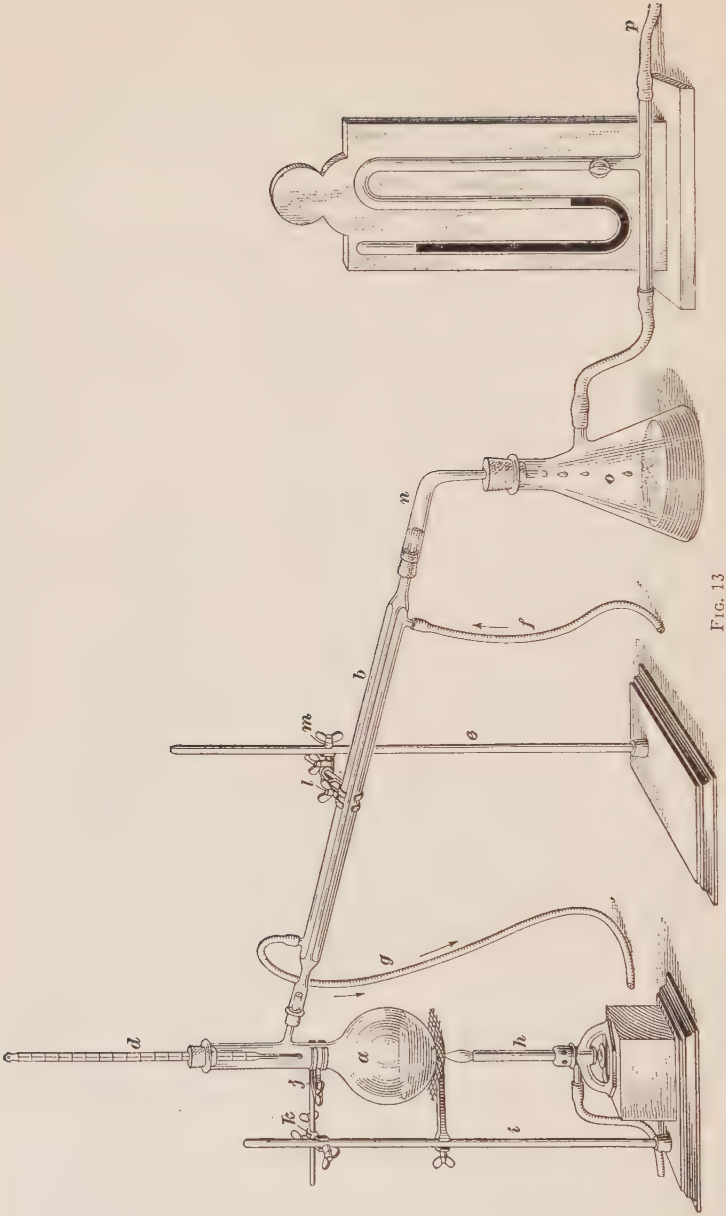


FIG. 13

phor, etc., which pass directly from a solid form to that of a vapor when heated without first forming liquids. The distillation of substances that condense directly into solids without forming liquids, is called sublimation and the condensed substances are called sublimates.

The process of sublimation is sometimes used to separate substances from one another. For example, if a mixture of sand and ammonium chloride is placed in a test tube and then heated dense white fumes of ammonium chloride are given off which upon cooling condense in the upper part of the tube as a white sublimate. The sand in the mixture is unaffected.

Substances that can be distilled, evaporated, or sublimed are called volatile and those that cannot be are called non-volatile bodies.

54. Ignition.—Some substances burn and form gases and others do not. This fact affords another means of separating substances that form a mixture. The substance that burns and generally forms a gas, called a combustible substance, passes from the mixture and leaves the substance that does not burn, called an incombustible substance, behind. The process of heating a substance intensely is called ignition.

As an example, suppose that charcoal and sand are to be separated from each other. If this mixture is heated to redness, the pure charcoal (carbon), a combustible substance, burns and forms a gas, carbon dioxide; the sand, an incombustible substance, remains behind.

55. Catalysis.—The term catalysis is given to a form of action by which a substance appears to exert a chemical effect without itself changing. Thus, hydrogen peroxide may be decomposed into water and oxygen by means of gold or silver, neither of which are altered in the least in the process of decomposition, but each exerts a catalytic action.

56. Effervescence, Deliquescence, Efflorescence. Effervescence is the escape of a gas from a liquid in which it is either generated or has been held by pressure, as carbonic acid obtained from dissolving marble or from soda water. Deliquescence is the dissolving of a substance in water which it absorbs

from the moisture present in the air. Examples are sodium and potassium hydroxides. Such substances are said to be hygroscopic, although all hygroscopic substances do not dissolve in the absorbed water. Efflorescence is the gradual crumbling of a crystal to powder on exposure to the air, due to the escape of the water necessary for the formation of the crystal. Examples are: copper sulphate, $CuSO_4{\cdot}5H_2O$, and ferrous sulphate, $FeSO_4{\cdot}7H_2O$.

METHOD OF WEIGHING

57. The Analytical Balance.—As a knowledge of the correct manipulation of an analytical balance is of importance to the chemist, a general description of the balance and its operation will be given at this point.

The balance illustrated in Fig. 14 (*a*) has a capacity of 200 grams and is sensitive to a weight of one-twentieth of a milligram. The balance is enclosed in a glass case fitted with sliding doors in front and in back. The drawer in the base contains the weights, brushes, spatula, etc. At the top of the hollow pillar *a* is embedded a rectangular-shaped piece *b* of agate, on which rest the agate knife edges *c* of the beam *d*. The stirrups *e*, from which the scale pans *f* are suspended, also rest on agate knife edges. At *g* is shown the leveling screw by which the case may be adjusted so as to bring the air bubble in the spirit level *h* into a central position.

The knob *i* operates a rod, placed in the pillar *a*, by means of which the beam may be lifted slightly off its bearings, or knife edges. This is the position to be occupied by the beam when the balance is not in use. By turning the knob *i* in the required direction, in this case to the left, the beam is lowered upon its knife edges and the balance is ready for weighing operations.

58. As the materials to be weighed have a more or less corrosive action on metals, the pans *f* carry balanced watch glasses on which the chemicals are placed. However, if noncorrosive solids are to be weighed, the pan at the left is provided with an aluminum scoop-shaped pan the weight of which

is exactly balanced by a special weight placed on the other pan. It is important to ascertain if the two pans are in perfect balance, in which case the pointer, or index, *j* should come to rest at the zero mark of the scale *k*, when the beam is released.

How far this is the case may be tested in the following manner: The balance is released by turning the knob *i* to the left; also, the scale pans are released by pushing in the knob *l* and turning it to the right. The beam and the pans are now free to swing and if the pointer moves over the same number of scale divisions on either side of the zero mark it indicates that the pans are in balance.

Should the pointer swing farther to the left of the zero mark, it proves that the right-hand pan is too heavy and that balance must be established by means of the screws *m* and *n*. In this case the screw *m* would be turned so as to bring it nearer the pillar *a*; or, the screw *n* would be turned in the same direction, thus bringing it farther away from *a*. Either of the screws should be given only a few turns at a time, testing the results and repeating the operations until the pointer swings over the same number of divisions on either side of the zero mark, coming finally to rest at this point.

Fig. 14 (*b*) is an enlarged view of the right-hand end of the beam partly broken away. In this view the rider *o* is clearly shown; also, the arm *p′* on the rod *p* by which the rider is moved into position. At the end of the beam is seen the adjusting screw *m*. At (*c*) is an end view of the beam, corresponding parts in all the views being indicated by similar letters.

59. The operation of weighing consists in placing the substance to be weighed on the left-hand watch glass and the required number of weights on the other glass to produce a balance between the two pans and thus compelling the pointer to come to rest at the zero mark. The smallest separate weight that may be used for the right-hand pan weighs 10 milligrams. In order to weigh closer than this, it is necessary to employ the platinum rider *o*, shown resting on the beam *d*, Fig. 14. This rider weighs 10 milligrams, and is known as a 10-milligram rider. When placed on the beam at the division marked *10*, it

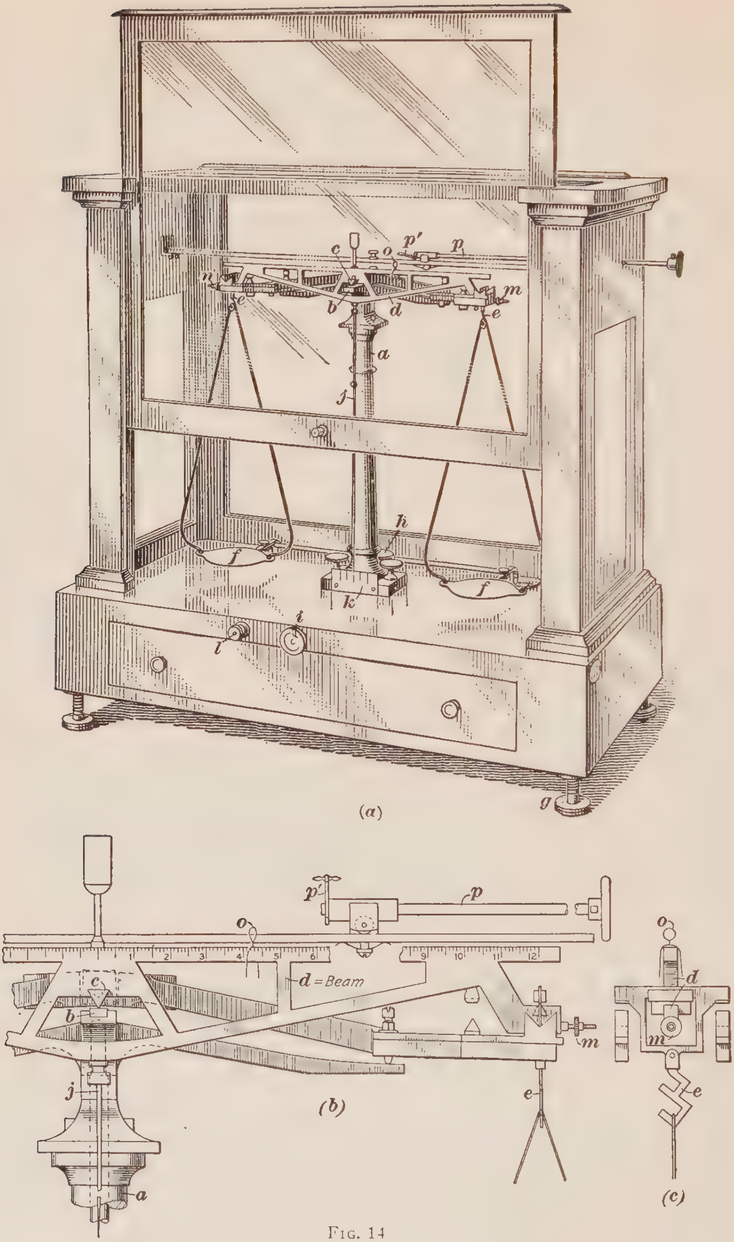


FIG. 14

produces the same effect as a 10-milligram weight placed on the right-hand pan. If this rider is moved to the division *1* of the beam or to any other division up to *12*, the effect produced corresponds with that obtained from placing a corresponding number of milligrams on the right-hand pan. In some balances there is a rider for each end of the beam and either one may be placed into position by means of the rods *p*.

60. The weights are usually kept in a box, as shown in Fig. 15. The larger weights are generally made of brass and sometimes gold-plated; the smaller ones are made of aluminum or platinum. Each small weight rests in a separate compart-

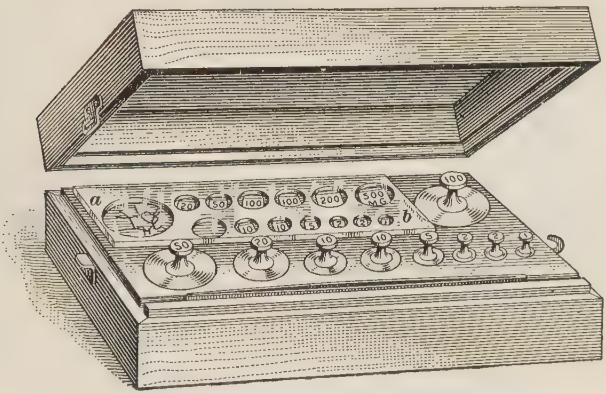


Fig. 15

ment under a glass lid *a b*. For the purpose of lifting the weights, a forceps is used, which has its place in the box.

Accurate weights must under no consideration be touched with the fingers, but always lifted with the forceps.

The arrangement of the weights varies with different makes. Fig. 15 shows the usual and most convenient arrangement for a set of weights of from 100 grams to .0001 gram.

Before attempting to weigh, the student must learn not only the denomination of each weight, but also its place in the box. He must be quite as well able to read the weights he has placed in the balance pan from the empty space in the box as from the weights themselves.

PRACTICAL HINTS

PHYSICAL OPERATIONS

61. Heating Glass.—Glass is one of the most useful of all materials to the chemist in his work, for it is transparent, can be put into different shapes when hot and plastic, and is unaffected by most chemicals. It is, however, brittle, a property that makes it liable to break, unless handled with care.

Heat should never be applied to glass unevenly lest the glass expand unevenly and crack. A wire gauze is used when heating liquids in glass vessels to keep the flame from coming into direct contact with the glass, and to secure an even distri-

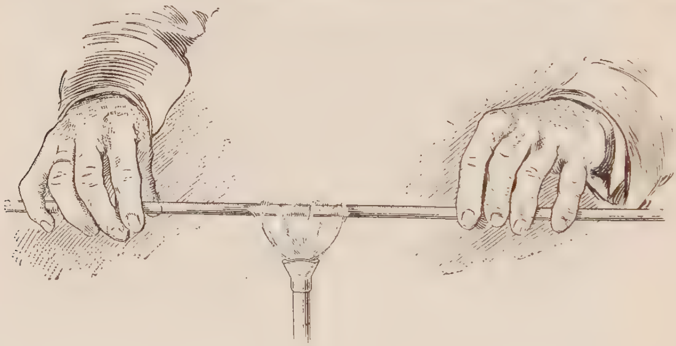


FIG. 16

bution of heat. In this way, equal expansion of all parts of the glass is obtained and there is little danger of the glass vessels cracking.

62. Bending and Drawing Glass Tubing.—Heat will make glass so soft that it can be bent into various shapes. Hold one end of the glass tube, to be bent, in each hand and place it lengthwise in a flat flame (generally produced by a fish-tail burner), as shown in Fig. 16; do not use the direct flame of the Bunsen burner for this work, for it will cause the glass to crease at the bend. Keep turning the glass slowly in the flame at the point where you wish to bend it until it softens and

begins to sag. Then raise the ends, as shown in Fig. 17, until the desired bend is obtained. Care should be taken to soften

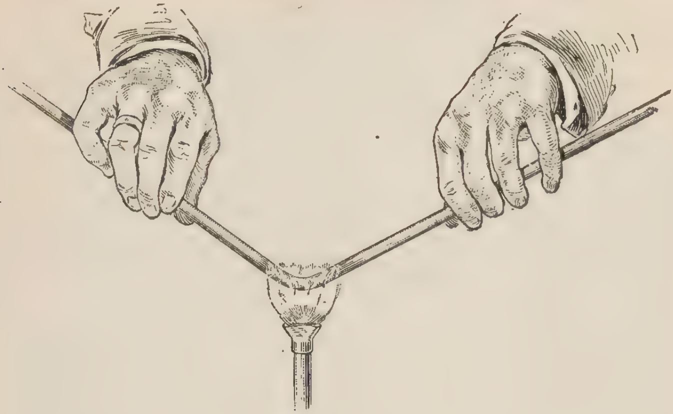


FIG. 17

the glass thoroughly before bending it; precautions should also be taken to keep turning the tube in the flame lest heat be applied to only one side, resulting in the bend being flat instead of even and round.

63. In order to make a capillary tube, as at *B A*, Fig. 18, a piece of glass tubing is heated at a middle point as in the foregoing operation. When it has softened remove the glass from the flame and draw the ends quickly in opposite directions. The tube will now appear as shown in Fig. 18, and the part of the tube between *A* and *B*, which has very thin walls and a small bore, may easily be broken out. This part of the tube is called a capillary tube and is used mostly for making melting point determinations, as will be shown later.

64. Cutting Glass Tubing.—A chemist often needs to cut a piece of glass tubing to a desired length, a task that is easily accomplished. Scratch the glass tube with a sharp, triangular

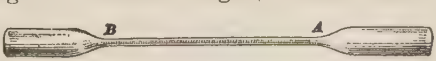


FIG. 18

file and then hold the tube in both hands; the two forefingers should be together immediately under the scratch and the two

thumbs above. Turn the wrists outwards and downwards, as though trying to widen the nick in the tubing, until the tube breaks. Fig. 19 illustrates this operation.

65. Rounding the Ends of Glass Tubing.—It is often necessary to round the sharp end of a piece of glass tubing so that it may be passed through rubber or cork stoppers without difficulty and inserted into rubber tubing without cutting the inside walls of the latter. The rounding is best accomplished by holding the sharp end in a Bunsen-burner flame until it begins to soften, at which time it becomes smooth and round. A moistened end will pass into a stopper or rubber tube more

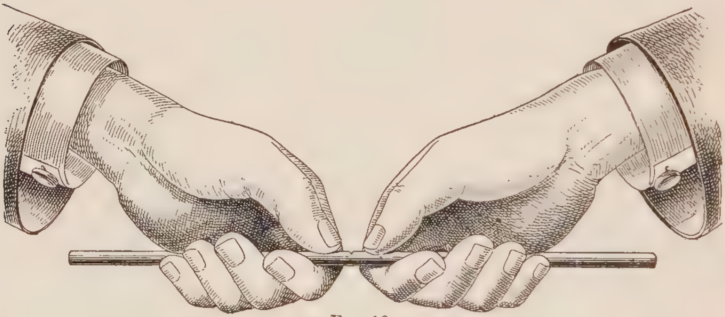


Fig. 19

readily than a dry one. For this reason, a little vaseline is sometimes rubbed around a tube end or it is dipped into water before it is inserted.

66. Boring Corks and Rubber Stoppers.—When apparatus is set up in the laboratory, it is generally necessary to use corks and rubber stoppers, and since these are sold in the solid form, unless otherwise specified, they must be bored in order to be used as shown in Figs. 11 and 13. For this purpose an instrument called a corkborer, Fig. 20, is used; it consists of a set of several thin metal (usually brass) tubes, the lower ends of which are sharpened. A rod is also contained in the set, in order to thrust out of the borer the piece of cork cut from the holes. The rod can also be pushed through two holes in the top of the borer, forming a handle to grasp when boring. Before commencing to bore, see that the borer is clear; then beginning

at the small end of the cork, bore carefully by twisting the borer and pushing it through. Take care, while this is going on, that the hole is perfectly straight. In order to insure a clean-cut hole at the point where the borer emerges from the cork, the latter may be placed over a block of soft wood so that when the borer comes through, the cork will be cut cleanly while, because of the soft wood, the instrument will not be dulled. The borer selected for the work should be just a trifle less in diameter than the glass tubing to be used. This will tend to produce an air-tight fitting. It will be found of advantage to wet the glass tube with water, in order to facilitate its passage through the hole in the cork. While attempting to force the glass tube into this hole the hand should be covered with a cloth as a protection in case the tube should break. Remember that the success of the experiment depends, to a large degree, on the fact that the stopper, as well as the glass tube, fits air-tight. Much time and trouble is saved by setting up every piece of apparatus as nearly perfect as possible.

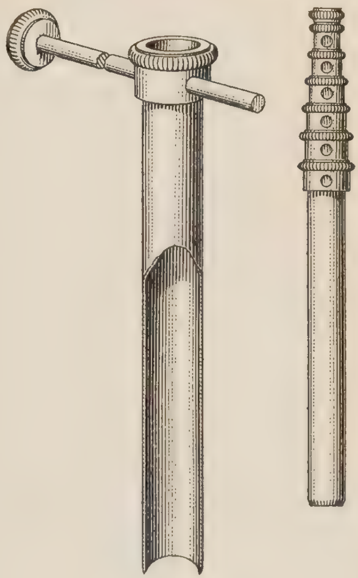


FIG. 20

On account of the difficulty in getting cork stoppers to fit air-tight, rubber stoppers are used in fitting up chemical apparatus, where the chemicals used do not attack the rubber.

INORGANIC CHEMISTRY
(PART 3)

CHEMICAL CALCULATIONS

PROPORTION, PERCENTAGE, AND CALCULATIONS OF QUANTITIES

INTRODUCTION

1. The Importance of Chemical Calculations. Chemists must know how to solve chemical problems, for they enter into all laboratory and industrial operations. Every test, made to determine the per cent. and quantity of a constituent in a material, can be completed only when one or more chemical problems have been solved, and every industrial operation in which chemistry is a factor, is based on definite quantities of materials that can be determined, theoretically, only by solving chemical problems. Unless one knows how to solve chemical problems with accuracy, his efforts will be of little value. It is, therefore, important that the methods of solving problems described at this point should be carefully studied and thoroughly understood.

PROPORTION

2. Fundamental Principles.—The mathematics involved in the solution of chemical problems consists essentially of the principles of proportion.

A **proportion** is an equality of ratios, the equality being indicated by the sign of equality (=). Thus, to write in the

form of a proportion the two equal ratios, 6 : 9 and 10 : 15, either one of the following forms may be employed:

$$6 : 9 = 10 : 15 \qquad (1)$$

$$\frac{6}{9} = \frac{10}{15} \qquad (2)$$

3. A proportion may be read in two ways. The old way to read the above proportion is, *6 is to 9 as 10 is to 15;* the new way is, *the ratio of 6 to 9 equals the ratio of 10 to 15.* Either way may be used, but the latter is recommended.

4. The numbers forming a proportion are called *terms*, and they are numbered consecutively from left to right, thus:

$$\overset{\textit{first}}{6} : \overset{\textit{second}}{9} = \overset{\textit{third}}{10} : \overset{\textit{fourth}}{15}$$

In any proportion the ratio of the first term to the second term equals the ratio of the third term to the fourth term.

The first and fourth terms of a proportion are called the *extremes*, and the second and third terms, the *means*. Thus, in the foregoing proportion, 6 and 15 are the extremes and 9 and 10 are the means.

5. The correctness of a proportion may be tested by applying the following rule:

Rule.—*In any proportion, the product of the extremes equals the product of the means.*

Thus, in the proportion, $6 : 9 = 10 : 15$, $6 \times 15 = 9 \times 10$, since both products equal 90.

If the proportion is written in the fractional form, as $\frac{6}{9} = \frac{10}{15}$, the term must be multiplied in the manner indicated by the diagonal lines, as follows: $\frac{6}{9} \times \frac{10}{15}$. Or, $6 \times 15 = 9 \times 10$. In either case, the result is the same.

6. Problems in Proportion.—The problem that most frequently occurs in proportion is to find one of the terms, when the other three terms are given. Suppose the ratio 6 : 13 is given, and, also the first term, 30, of the second ratio, which term is the third term of the proportion and one of the means.

The unknown term in a proportion is usually indicated by the letter x. The given ratios may therefore be written as the following proportion:

$$6 : 13 = 30 : x$$

The unknown extreme x may be found by the following rule:

Rule.—*To find an unknown extreme, divide the product of the means by the given extreme.*

Applying this rule to the preceding example,

$$x = \frac{13 \times 30}{6} = \frac{390}{6} = 65$$

7. If the unknown quantity is one of the mean terms, the following rule applies:

Rule.—*To find an unknown mean, divide the product of the extremes by the given mean.*

EXAMPLE.—The two ratios 17 : 51 and x : 42 are given. What is the value of the unknown term x?

SOLUTION.—In this example, the terms 17 and 42 are the extremes, and 51 the given mean. Applying the rule,

$$x = \frac{17 \times 42}{51} = 14. \quad \text{Ans.}$$

8. In certain branches of chemical calculations a proportion is preferably stated in the form of a ratio, as $\frac{3}{9} = \frac{x}{36}$, x being the unknown quantity, as before. Applying the method explained in Art. 5, the following equation is obtained: $3 \times 36 = 9 \times x$. In order that the unknown quantity x may stand alone on one side of the equality sign, both sides of the equation are divided by 9; thus, $\frac{3 \times 36}{9} = \frac{9x}{9} = x$.

Or, $$x = \frac{3 \times 36}{9} = 12$$

PERCENTAGE CALCULATIONS

9. Advantage of Percentage Calculations.—In certain operations pertaining to chemistry, it is very convenient to consider the quantity under consideration as being divided into 100 equal parts. Thus, instead of using the ordinary fractions $\frac{1}{4}$, $\frac{3}{5}$, and $\frac{2}{7}$, the equivalent fractions $\frac{25}{100}$, $\frac{60}{100}$, and $\frac{28\frac{4}{7}}{100}$ are used, or their equivalent decimals, .25, .60, and .286, respectively. The reason for this is that it is much easier to compute with fractions whose denominators are 100 than it is to compute with fractions whose denominators are composed of other figures.

10. Definitions.—**Percentage** is a term applied to those arithmetical operations in which the number or quantity to be operated upon is supposed to be divided into 100 equal parts.

The term *per cent.* means *by the hundred*. Thus, 8 per cent. of a number means 8 hundredths, that is, $\frac{8}{100}$, or .08, of that number; 8 per cent. of 250 is $250\times\frac{8}{100}$, or $250\times.08=20$; 47 per cent. of 75 ounces is $75\times\frac{47}{100}=75\times.47=35.25$ ounces.

The sign of the per cent. is %, and is read *per cent.* Thus, 6% is read *six per cent.*; $12\frac{1}{2}$% is read *twelve and one-half per cent.*, etc.

When expressing the per cent. of a number used in calculations, it is customary to express it decimally instead of fractionally. Thus, instead of expressing 6%, 25%, and 43% as $\frac{6}{100}$, $\frac{25}{100}$, and $\frac{43}{100}$, it is usual to express them as .06, .25, and .43, respectively.

11. Use of Atomic Weights in Problems.—Atomic weights are used to calculate the relative quantities, called combining weights, in which elements enter into compounds and in which substances enter into chemical changes. All chemical problems are based on the law of definite proportion, which states, as mentioned elsewhere in *Inorganic Chemistry* that *a chemical compound always contains the same constituents in the same proportion by weight.*

Consider, for example, water, the formula of which is H_2O. This formula shows that each molecule of water contains 2 atoms of hydrogen and 1 atom of oxygen. This fact is always true for water. By means of the atomic weights of these elements, one can calculate the weight relation between oxygen and hydrogen in water. The atomic weight of hydrogen, as shown in Table I, is 1.008, and that of oxygen is 16. The molecular weight of water is $(2 \times 1.008) + 16$, or 18.016. These values show that every 18.016 parts* of water contain 2.016 parts of hydrogen and 16 parts of oxygen. That is, the weight ratio of hydrogen to oxygen, in water, is 2.016 : 16, and 2.016 parts of hydrogen are needed to combine chemically with 16 parts of oxygen to produce 18.016 parts of water.

These parts by weight can be expressed in terms of any weight unit, such as grams, pounds, tons, kilograms, etc. For instance, when grams are used every 18.016 grams of water contain 2.016 grams of hydrogen and 16 grams of oxygen; 2.016 grams of hydrogen unite with 16 grams of oxygen to produce 18.016 grams of water, and the ratio of hydrogen to oxygen in 18.016 grams of water is 2.016 grams : 16 grams.

These various weight relations based on the atomic weights of elements are used, as will be shown, in the solution of chemical problems.

12. Calculating Per Cents. of Constituents in a Compound.—A chemist must often calculate the per cent. of a constituent in a substance, using as a basis his knowledge of the chemical formula of the compound under consideration. He does this by applying atomic and molecular weights to the mathematical operations involved in calculating all percentages.

For illustration, suppose it is required to calculate the percentages of hydrogen and oxygen contained in water. By consulting a table of atomic weights it is found that the atomic weight of hydrogen is 1.008 and that of oxygen is 16. These facts afford a basis for calculating the molecular weight of water. Each molecule of water consists of 2 atoms of hydro-

*The term *parts* will, unless otherwise specified, refer to *parts by weight.*

TABLE I

INTERNATIONAL ATOMIC WEIGHTS, 1925

Name	Symbol	Atomic Weight	Name	Symbol	Atomic Weight
Aluminum........	*Al*	26.97	Mercury (Hydrargyrum)..	*Hg*	200.61
Antimony (Stibium)......	*Sb*	121.77	Molybdenum......	*Mo*	96.0
Argon............	*A*	39.91	Neodymium.......	*Nd*	144.27
Arsenic...........	*As*	74.96	Neon............	*Ne*	20.2
Barium...........	*Ba*	137.37	Nickel...........	*Ni*	58.69
Bismuth..........	*Bi*	209.0	Nitrogen.........	*N*	14.008
Boron............	*B*	10.82	Osmium..........	*Os*	190.8
Bromine..........	*Br*	79.916	Oxygen..........	*O*	16.0
Cadmium.........	*Cd*	112.41	Palladium.........	*Pd*	106.7
Cæsium...........	*Cs*	132.81	Phosphorus.......	*P*	31.027
Calcium..........	*Ca*	40.07	Platinum.........	*Pt*	195.23
Carbon...........	*C*	12.0	Potassium (Kalium)	*K*	39.096
Cerium...........	*Ce*	140.25	Praseodymium....	*Pr*	140.92
Chlorine..........	*Cl*	35.457	Radium..........	*Ra*	225.95
Chromium........	*Cr*	52.01	Radon (Niton)....	*Rn*	222
Cobalt...........	*Co*	58.94	Rhodium.........	*Rh*	102.91
Columbium.......	*Cb*	93.1	Rubidium.........	*Rb*	85.44
Copper (Cuprum)..	*Cu*	63.57	Ruthenium........	*Ru*	101.7
Dysprosium.......	*Dy*	162.52	Samarium.........	*Sa*	150.43
Erbium...........	*Er*	167.7	Scandium.........	*Sc*	45.1
Europium.........	*Eu*	152.0	Selenium..........	*Se*	79.2
Fluorine..........	*F*	19.0	Silicon...........	*Si*	28.06
Gadolinium.......	*Gd*	157.26	Silver (Argentum).	*Ag*	107.88
Gallium..........	*Ga*	69.72	Sodium (Natrium).	*Na*	22.997
Germanium.......	*Ge*	72.6	Strontium.........	*Sr*	87.63
Glucinum (Beryllium)...........	*Gl*	9.02	Sulphur..........	*S*	32.064
			Tantalum.........	*Ta*	181.5
Gold (Aurum).....	*Au*	197.2	Tellurium........	*Te*	127.5
Hafnium..........	*Hf*	180.8	Terbium..........	*Tb*	159.2
Helium...........	*He*	4.0	Thallium.........	*Tl*	204.39
Holmium.........	*Ho*	163.4	Thorium..........	*Th*	232.15
Hydrogen.........	*H*	1.008	Thulium..........	*Tm*	169.4
Indium...........	*In*	114.8	Tin (Stannum)....	*Sn*	118.7
Iodine............	*I*	126.932	Titanium.........	*Ti*	48.1
Iridium...........	*Ir*	193.1	Tungsten.........	*W*	184.0
Iron (Ferrum).....	*Fe*	55.84	Uranium..........	*U*	238.17
Krypton..........	*Kr*	82.9	Vanadium........	*V*	50.96
Lanthanum.......	*La*	138.9	Xenon...........	*Xe*	130.2
Lead (Plumbum)..	*Pb*	207.2	Ytterbium (Neoytterbium).	*Yb*	173.6
Lithium..........	*Li*	6.94			
Lutecium.........	*Lu*	175.0	Yttrium..........	*Yt*	88.9
Magnesium.......	*Mg*	24.32	Zinc..............	*Zn*	65.38
Manganese.......	*Mn*	54.93	Zirconium........	*Zr*	91.0

gen and 1 atom of oxygen. The molecular weight is, therefore, $(2 \times 1.008)+16$, or 18.016.

He next calculates the amount of one of the constituents present, as for instance, hydrogen. He knows from the atomic and molecular weights that 18.016 parts of water contain 2.016 parts of hydrogen. In this case the 18.016 parts of water represent the total weight of the compound and the 2.016 parts represent the weight of hydrogen. The per cent. of hydrogen represented by this quantity may be calculated as follows: $\frac{2.016 \times 100}{18.016} = 11.19$ per cent. That is, in 100 parts of water there are 11.19 parts of hydrogen.

The per cent. of oxygen is calculated in the same manner. Thus, $\frac{16 \times 100}{18.016} = 88.81$ per cent. of oxygen. That is, water contains 88.81 per cent. of oxygen.

13. The method used for calculating the per cent. of hydrogen and of oxygen contained in water is applied to all similar problems. But, it may be modified so as to apply more directly to a special class of problems. This modified method may be stated as a rule as follows:

Rule.—*To find the per cent. by weight of an element in a chemical compound, multiply the atomic weight of the element by the number of atoms of that element in a molecule of the compound and also by 100, and then divide the product by the molecular weight of the substance.*

EXAMPLE.—The formula for potassium chlorate is $KClO_3$. What is the per cent. of each element in the compound?

SOLUTION.—It is first necessary to find the molecular weight of the compound.

Each molecule of $KClO_3$ contains 1 atom of potassium, 1 of chlorine, and 3 of oxygen. Hence, the molecular weight is calculated by means of the atomic weights of the elements, as follows:

$1 \times 39.10 = 39.10$, for potassium
$1 \times 35.46 = 35.46$, for chlorine
$3 \times 16.00 = 48.00$, for oxygen
Total, 122.56 = molecular weight of potassium chlorate

Then by the preceding method, the per cent. of each element is found in the following manner:

$$\text{Per cent. of potassium} = \frac{1 \times 39.10 \times 100}{122.56} = \frac{3{,}910.00}{122.56} = 31.90, \text{ nearly. Ans.}$$

$$\text{Per cent. of chlorine} = \frac{1 \times 35.46 \times 100}{122.56} = \frac{3{,}546.00}{122.56} = 28.93, \text{ nearly. Ans.}$$

$$\text{Per cent. of oxygen} = \frac{3 \times 16.00 \times 100}{122.56} = \frac{4{,}800.00}{122.56} = 39.17, \text{ nearly. Ans.}$$

The calculation may be checked by finding the sum of the various per cents., which should always be approximately equal to 100.

Example 2.—Ferric oxide has the formula Fe_2O_3. What per cent. of iron is present in the compound?

Solution.—Each molecule of ferric oxide contains 2 atoms of iron and 3 of oxygen. The molecular weight is, therefore, found as follows:

$$\begin{aligned} 2 \times 55.84 &= 111.68, \text{ for iron} \\ 3 \times 16.00 &= \underline{\ \ 48.00}, \text{ for oxygen} \\ \text{Total,} \quad & \ \ 159.68 = \text{molecular weight of ferric oxide} \end{aligned}$$

The per cent. of iron is,

$$\frac{2 \times 55.84 \times 100}{159.68} = \frac{11{,}168.00}{159.68} = 69.94, \text{ nearly. Ans.}$$

Example 3.—What per cent. of copper is contained in copper sulphate, $CuSO_4 \cdot 5H_2O$?

Solution.—Each molecule of copper sulphate contains 1 atom of copper, 1 of sulphur, 9 of oxygen, and 10 of hydrogen. The molecular weight is, therefore, as follows:

$$\begin{aligned} 1 \times 63.57 &= \ \ 63.57, \text{ for copper} \\ 1 \times 32.06 &= \ \ 32.06, \text{ for sulphur} \\ 9 \times 16.00 &= 144.00, \text{ for oxygen} \\ 10 \times \ 1.008 &= \underline{\ \ 10.08}, \text{ for hydrogen} \\ \text{Total,} \quad & \ \ 249.71 = \text{molecular weight of copper sulphate} \end{aligned}$$

The per cent. of copper is found thus, $\dfrac{1 \times 63.57 \times 100}{249.71} = 25.46$, nearly. Ans.

14. It is sometimes necessary to calculate the per cent. of a constituent consisting of more than one element. In such cases the molecular weight of the constituent is used in the calculation. The following examples will illustrate the method to be followed:

Example 1.—Calculate the per cent. of calcium oxide, or lime, CaO, contained in calcium carbonate, $CaCO_3$.

SOLUTION.—The molecular weight of calcium carbonate is found in the manner previously described. Thus,

$$\begin{array}{rl} 1\times 40.070 = & 40.070, \text{ for calcium} \\ 1\times 12.005 = & 12.005, \text{ for carbon} \\ 3\times 16.000 = & \underline{48.000}, \text{ for oxygen} \\ \text{Total,} & 100.075 = \text{molecular weight of calcium carbonate} \end{array}$$

The molecular weight of calcium oxide must also be found. Thus,

$$\begin{array}{rl} 1\times 40.070 = & 40.070, \text{ for calcium} \\ 1\times 16.000 = & \underline{16.000}, \text{ for oxygen} \\ \text{Total,} & 56.070 = \text{molecular weight of calcium oxide} \end{array}$$

Thus, the per cent. of calcium oxide in calcium carbonate is:

$$\frac{56.07\times 100}{100.075} = 56.03, \text{ nearly.} \quad \text{Ans.}$$

EXAMPLE 2.—Calculate the per cent. of carbon dioxide, CO_2, in sodium carbonate, Na_2CO_3.

SOLUTION.—The molecular weight of sodium carbonate is found in the following manner:

$$\begin{array}{rl} 2\times 23.00 \;= & 46.000, \text{ for sodium} \\ 1\times 12.005 = & 12.005, \text{ for carbon} \\ 3\times 16.000 = & \underline{48.000}, \text{ for oxygen} \\ \text{Total,} & 106.005 = \text{molecular weight of sodium carbonate} \end{array}$$

The molecular weight of carbon dioxide is:

$$\begin{array}{rl} 1\times 12.005 = & 12.005, \text{ for carbon} \\ 2\times 16.000 = & \underline{32.000}, \text{ for oxygen} \\ \text{Total,} & 44.005 = \text{molecular weight of carbon dioxide} \end{array}$$

Applying the method, the per cent. of carbon dioxide is

$$\frac{44.005\times 100}{106.005} = 41.51, \text{ nearly.} \quad \text{Ans.}$$

EXAMPLE 3.—Calculate the per cent. of phosphorus pentoxide, P_2O_5, contained in sodium phosphate, $Na_2HPO_4 \cdot 12H_2O$.

SOLUTION.—The principle involved in finding the per cent. of a group of atoms is the same as that used in finding the per cent. of a single atom. In the formula $Na_2HPO_4 \cdot 12H_2O$, there is only 1 atom of phosphorus while the compound P_2O_5 contains 2 atoms of phosphorus. Therefore, in order to find the per cent. of phosphorus pentoxide in sodium phosphate, the formula for the latter must be multiplied by 2. Thus we have $2Na_2HPO_4 \cdot 12H_2O$. The per cent. of P_2O_5 may now be found in the usual manner but in order to simplify the problem as much as possible, the multiplication as indicated by the coefficient 2, is first carried out and the formula becomes,

$Na_4H_2P_2O_8 \cdot 24H_2O$. Then taking up each atom in regular order, beginning with sodium, the molecular weight is calculated as follows:

$$\begin{array}{rl} 4\times 23.000 = & 92.000 \text{ for sodium} \\ 2\times 1.008 = & 2.016 \text{ for hydrogen} \\ 2\times 31.040 = & 62.080 \text{ for phosphorus} \\ 8\times 16.000 = & 128.000 \text{ for oxygen} \\ 48\times 1.008 = & 48.384 \text{ for hydrogen} \\ 24\times 16.000 = & 384.000 \text{ for oxygen} \\ \text{Total,} & 716.480 \end{array}$$

The molecular weight of P_2O_5 is:

$$\begin{array}{rl} 2\times 31.04 = & 62.08, \text{ for phosphorus} \\ 5\times 16.00 = & 80.00, \text{ for oxygen} \\ \text{Total,} & 142.08 \end{array}$$

The per cent. of P_2O_5 is:

$$\frac{142.08\times 100}{716.48} = 19.8. \quad \text{Ans.}$$

CALCULATING QUANTITIES OF CONSTITUENTS

15. To Calculate Quantities in Chemical Problems. Chemists are required to calculate the quantities of substances needed to produce certain chemical changes and the quantities of the products formed. Chemical equations representing the changes are used as a basis for these calculations, and as they must be properly written, if the calculation is to be correct, a review of the methods for ascertaining whether an equation is correct, will, at this point, be helpful.

First of all, a chemical equation is not correct unless it represents a change that actually takes place and can be reproduced. Likewise, the quantities by weight of the materials which react, can never be greater nor less than the quantities by weight of the materials produced, for matter can be neither created nor destroyed. In other words, the sum of the combining weights, calculated from the atomic weights of the elements involved, on one side of the equation must equal the sum of the combining weights on the other. Finally, the number of atoms of any element on one side of an equation must equal the number of atoms of that element on the other side. If a chemical equation meets all of these requirements, it is correctly written and can

be used as a basis for the calculation of quantities involved in chemical changes.

As an illustration, consider the change that takes place when magnesium, Mg, is burned to form magnesium oxide, MgO. The valence of magnesium is 2 and that of oxygen is 2. Hence, 1 atom of magnesium is needed to unite with 1 atom of oxygen, thus:

$$Mg+O=MgO$$

This equation is not correct, however, because oxygen always exists in nature as a molecule, O_2, and not as an atom, O, as shown in this equation. Doubling the quantities in the equation will show oxygen as a molecule, thus:

$$2Mg+O_2=2MgO$$

16. The combining weights, atomic or molecular, of the substances used and produced are next calculated from the atomic weights of the various elements involved. As the atomic weight of magnesium $=24.32$, it follows that 2 atoms of magnesium, $2Mg$, have a combining weight of $2\times24.32=48.64$. The atomic weight of oxygen $=16$; then 2 atoms of oxygen contained in 1 molecule of oxygen, O_2, have a combining weight of 32.00. The molecular weight of magnesium oxide, containing 1 atom of magnesium and 1 of oxygen, equals the sum of the atomic weights of magnesium and oxygen, 24.32 and 16, or 40.32. The equation shows 2 molecules of magnesium oxide; it has a combining weight, therefore, of 2×40.32, or 80.64.

The combining weights of the substances involved in a chemical change are, for convenience, placed under the respective formulas and symbols of the substances, thus:

$$\begin{array}{c} 2Mg + O_2 = 2MgO \\ 48.64 + 32.00 = 80.64 \end{array}$$

This equation shows that 48.64 parts by weight of magnesium unite with 32.0 parts of oxygen to form 80.64 parts of magnesium oxide; that 32.0 parts of oxygen unite with 48.64 parts of magnesium to produce magnesium oxide; that 48.64 parts of magnesium form 80.64 parts of magnesium oxide when burned; that the sum of the weights of magnesium and oxygen, combined chemically, equals the weight of magnesium oxide formed.

17. So far, the equation $2Mg+O_2=2MgO$ has met two of the requirements of a correctly written chemical equation; it represents a change that can be produced by burning magnesium and the sum of the combining weights on one side of the equation is equal to that on the other. Likewise, it meets the third requisite for there are 2 atoms of magnesium and 2 of oxygen on each side of the equation. Hence, the equation is correctly written and can be used as a basis for calculations involving the chemical combination between magnesium and oxygen.

For instance, a chemist may be asked how much magnesium oxide is produced when 100 pounds of magnesium are burned. Such problems are based primarily on the fact that the combining weights of substances entering into a change are directly proportional to the exact quantities of these substances. This fact can be expressed as a proportion, thus:

The ratio of the combining weight of one substance to its weight equals the ratio of the combining weight of the substance formed to its weight.

In the process of burning magnesium to form magnesium oxide, the ratios representing the reaction may be written as follows:

$$\begin{array}{lcl} 48.64 & & 80.64 \\ 2Mg & +O_2= & 2MgO \\ 100\text{ lb.} & & x \end{array}$$

When the reaction that takes place and the values of the combining weights are represented in this manner, it is a simple matter to write the correct proportion. In the preceding statement representing the reaction, there are two ratios which are to form a proportion. Arranging these ratios as a proportion, it will assume the following form: $\frac{48.64}{100}=\frac{80.64}{x}$.

Solving the proportion according to the method previously given, the following equation is obtained:

$$48.64x=80.64\times 100$$

$$x=\frac{80.64\times 100}{48.64}=165.79\text{ lb. of } MgO. \quad \text{Ans.}$$

If preferred, the ratios $\frac{48.64}{100}=\frac{80.64}{x}$ may be arranged as in the following proportion:

$$48.64 : 100 = 80.64 : x$$

And the value of x found as follows:

$$x=\frac{80.64\times 100}{48.64}=165.79 \text{ lb. of } MgO. \quad \text{Ans.}$$

18. General Method for Solving Problems Involving Weights.—The calculation of weights of elements and compounds involved in chemical changes may be simplified by performing the various steps of the calculation in the following order:

1. Write the chemical equation representing the change. It should be noted that some equations may be written by applying the valence principles. Others that represent reactions not following the general rule, must be written from memory or secured from textbooks. In every case, an equation represents merely a change that has been shown by experimental work to take place.

2. Check the accuracy of the equation by noting whether it meets all the requirements of a correctly written equation.

3. Calculate the combining weights of the substances involved in the problem and place these weights over the proper symbols in the equation.

4. Arrange the known and the unknown values as ratios and calculate the unknown value by means of the rules of proportion.

19. The application of the preceding method of calculation will be shown by the following examples:

Example 1.—Calculate the weights of sodium chloride, $NaCl$, and sulphuric acid, H_2SO_4, required to produce 100 kilograms of sodium sulphate, Na_2SO_4.

Solution.—The first step in the solution of the problem is to write the equation representing the reaction. Thus,

$$2NaCl+H_2SO_4=Na_2SO_4+2HCl$$

It is seen that three substances—sodium chloride, sulphuric acid, and sodium sulphate—are in the solution of the problem, the fourth substance, hydrochloric acid, HCl, being left out of consideration, as it is not required.

According to Art. **18**, the next step is to calculate the combining weights of the substance and place them over the corresponding formula in the equation. Thus,

$$\overset{116.92}{2NaCl}+\overset{98.076}{H_2SO_4}=\overset{142.06}{Na_2SO_4}+2HCl$$

The required weight of sodium sulphate is 100 kilograms, so this weight is written under its formula in the equation. As the weights of the sodium chloride and the sulphuric acid are to be found, these weights are, for the present, indicated by the symbols x and x_1 in the equation. In its present form the equation will appear as follows:

$$\underset{x}{\overset{116.92}{2NaCl}}+\underset{x_1}{\overset{98.076}{H_2SO_4}}=\underset{100\text{ kg.}}{\overset{142.06}{Na_2SO_4}}+2HCl$$

Omitting the formulas, for reasons of clearness, the given ratios may be stated in the following manner:

$$\frac{116.92}{x},\ \frac{98.076}{x_1},\ \text{and}\ \frac{142.06}{100}$$

Each one of the unknown ratios is now combined with the known ratio, $\frac{142.06}{100}$, as a proportion in order to find the values of x and x_1.

Thus, to calculate the weight of sodium chloride required, the following proportion is written:

$$\frac{116.92}{x}=\frac{142.06}{100}$$

Solving, $142.06x=116.92\times100$.

$$x=\frac{116.92\times100}{142.06}=82.3\text{ kg. of } NaCl$$

Similarly, to calculate the weight of the sulphuric acid, the second ratio is employed.

Thus,

$$\frac{98.076}{x_1}=\frac{142.06}{100}$$

$$142.06x_1=98.076\times100$$

$$x_1=\frac{98.076\times100}{142.06}=69.04\text{ kg. of } H_2SO_4$$

It follows that to produce 100 kg. of sodium sulphate there are required 82.3 kg. of sodium chloride and 69.04 kg. of sulphuric acid. Ans.

Example 2.—Potassium acid sulphate, $KHSO_4$, in addition to nitric acid may be produced by adding sulphuric acid to potassium nitrate, KNO_3. If 500 grams of H_2SO_4 are available, how many grams of $KHSO_4$ may be produced, and how many grams of KNO_3 are required?

SOLUTION.—The formula, together with the combining weights, the unknown terms, and the given term, are written as in the last example.

Thus,
$$\overset{101.11}{\underset{x_1}{KNO_3}}+\overset{98.076}{\underset{500\text{ g.}}{H_2SO_4}}=\overset{136.168}{\underset{x}{KHSO_4}}+HNO_3$$

The three ratios may be written,

$$\frac{136.168}{x},\ \frac{101.11}{x_1},\ \text{and}\ \frac{98.076}{500}$$

Combining each unknown ratio in turn with the known one, the following proportions may be written:

$$\frac{136.168}{x}=\frac{98.076}{500}$$

and
$$\frac{101.11}{x_1}=\frac{98.076}{500}$$

It follows that $98.076x=136.168\times500$.

$$x=\frac{136.168\times500}{98.076}=694.19\text{ g.}$$

Also,
$$98.076x_1=101.11\times500$$

$$x_1=\frac{101.11\times500}{98.076}=515.46\text{ g.}$$

Hence, if 515.46 g. of potassium nitrate are added to 500 g. of sulphuric acid, 694.19 g. of potassium acid sulphate are produced. Ans.

EXAMPLE 3.—How many grams of silver, Ag, can be obtained from 1,000 grams of silver sulphate, Ag_2SO_4?

SOLUTION.—The molecular weight of Ag_2SO_4 is 311.82. The atomic weight of Ag is 107.88. It follows that $2Ag=107.88\times2=215.76$. The formulas, with the corresponding molecular weights, as well as the required weight of silver sulphate, are as follows:

$$\overset{311.82}{\underset{1{,}000\text{ grams}}{Ag_2SO_4}}\text{——}\overset{215.76}{\underset{x}{2Ag}}$$

The following ratios may now be written:

$$\frac{311.82}{1{,}000}=\frac{215.76}{x}$$

Hence,
$$311.82x=215.76\times1{,}000$$

$$x=\frac{215.76\times1{,}000}{311.82}=691.94\text{ g.}\quad\text{Ans.}$$

20. To Find the Formula of a Substance.—Chemists are occasionally required to calculate the formula of a compound, from the per cents. of the various elements in the com-

pound. For example, sulphuric acid was found on analysis to contain 2.05 per cent. of hydrogen, 32.68 per cent. of sulphur, and 65.27 per cent. of oxygen. In the calculation of the formula, the atomic weight of each element is divided into the percentage of that element in the compound, thus:

$2.05 \div 1.008 = 2.03$ for hydrogen
$32.68 \div 32.06 = 1.02$ for sulphur
$65.27 \div 16.00 = 4.08$ for oxygen

The quotient is in each case divided by the smallest one, in this case 1.02, thus:

$2.03 \div 1.02 = 2$, number of atoms of hydrogen present
$1.02 \div 1.02 = 1$, number of atoms of sulphur present
$4.08 \div 1.02 = 4$, number of atoms of oxygen present

The formula is, therefore, H_2SO_4.

The rule for finding the formula of a compound, using the percentages of the elements present as a basis is:

Rule.—*Divide the atomic weight of each element into the percentage of that element in the compound, and then divide each quotient by the smallest quotient to find the number of atoms of each element in the compound.*

Following are more examples showing application of this rule:

EXAMPLE 1.—Water was found to contain 11.19 per cent. of hydrogen and 88.81 per cent. of oxygen. What is the formula of water?

SOLUTION.—By dividing the percentage of each element by its atomic weight, we have

$11.19 \div 1.008 = 11.10$
$88.81 \div 16 = 5.55$

By dividing each quotient by the smallest quotient, we have

$11.10 \div 5.55 = 2$ atoms of hydrogen in water
$5.55 \div 5.55 = 1$ atom of oxygen in water

The formula of water is, therefore, H_2O.

EXAMPLE 2.—A chemist found on analysis that a substance contained 3.08 per cent. of hydrogen, 31.65 per cent. of phosphorus, and 65.27 per cent. of oxygen. What was the formula of the material?

SOLUTION.—By dividing the percentage of each element by its atomic weight, we have

$3.08 \div 1.008 = 3.05$ for hydrogen
$31.65 \div 31.04 = 1.01$ for phosphorus
$65.27 \div 16 = 4.08$ for oxygen

By dividing each quotient by the smallest quotient, we have

$3.05 \div 1.01 = 3+$, number of atoms of hydrogen present
$1.01 \div 1.01 = 1$, number of atoms of phosphorus present
$4.08 \div 1.01 = 4+$, number of atoms of oxygen present

Hence, the formula of the substance is H_3PO_4, and the chemist was able to decide that he had tested phosphoric acid, for which this formula stands.

21. Solution of Problems Involving Gases.—Volumes of gases, as well as weights of materials, may enter into chemical problems. In problems involving gases, temperature, pressure, and density are important factors. For example, a chemical change may result in the production of a gas, the volume of which must be determined. Problems of this nature are solved by converting gaseous volumes to weight equivalents and weights of gases to volume.

Two general methods may be used for finding the weight of a liter of any gas.

1. The weight of a liter of gas may be obtained by multiplying its density, which may be taken as one-half of its molecular weight, by the weight of 1 liter of hydrogen at a temperature of 0° C. and a pressure of 760 millimeters. The weight of 1 liter of hydrogen at this temperature and pressure may be taken as .089873 gram.

The molecular weight of hydrogen sulphide, H_2S, is 34; its approximate density is 17; therefore, the weight of 1 liter of H_2S may be obtained as follows:

$$17 \times .089873 = 1.527 \text{ grams}$$

2. The approximate weight of a liter of any gas may also be calculated by the use of the following rule:

The molecular weight of a gas at 0° C. and 760 millimeters pressure, is contained in 22.4 liters of the gas.

The molecular weight of H_2S is 34, and 34 grams of H_2S are approximately contained in 22.4 liters of gas. Then, 1 liter of H_2S would weigh $34 \div 22.4 = 1.517$ grams. Any slight difference in results, obtained by the use of the two methods, is negligible.

The molecular weight of oxygen is 32, and 32 grams are contained in 22.4 liters. Then, 1 liter would weigh $32 \div 22.4 = 1.428$ grams.

Case I.—*To find the volume of gaseous product at normal temperature and pressure or 0° C. and 760 millimeters.*

EXAMPLE.—What volume of oxygen gas at normal temperature and pressure can be obtained from 30 grams of potassium chlorate, $KClO_3$?

SOLUTION.—The equation representing the reaction should first be written

$$\underset{30}{\frac{245}{2KClO_3}} = 2KCl + \underset{x}{\frac{96}{3O_2}}$$

Then,
$$\frac{245}{30} = \frac{96}{x}$$

Or,
$$245x = 96 \times 30$$

and,
$$x = \frac{96 \times 30}{245} = 11.75 \text{ grams of oxygen}$$

One liter of oxygen weighs $16 \times .089873$ gram $= 1.44$ grams. Then, $11.75 \div 1.44 = 8.159$ liters of oxygen.

Case II.—*To find the volume of a gas at other than normal temperature, the pressure remaining constant.*

The law of Charles or Gay-Lussac may be stated as follows: *The volume of a gas varies as the temperature.* In other words, if the temperature of a certain volume of gas is increased, the volume which the gas will occupy will also increase in direct proportion to the rise in temperature, and the reverse holds true if the temperature of a certain volume of gas is decreased. This law may be expressed by the proportion:

$$\frac{V}{V'} = \frac{T}{T'}$$

in which V = original volume;
V' = new volume;
$T = (273+t)$ = original temperature;
$T' = (273+t')$ = new temperature.

EXAMPLE.—A gas occupies 200 liters at 50° C. What volume will it occupy at −5° C.?

SOLUTION.—From the above proportion we get

$$V'T = VT' \text{ or } V' = \frac{VT'}{T}$$

By substitution in this formula,

$$V' = \frac{200 \times (273-5)}{273+50} = \frac{200 \times 268}{323} = 165.94 \text{ liters}$$

Case III.—*To find the volume of a gas at other than normal pressure, the temperature remaining constant.*

Boyle's law may be stated as follows:

The volume of a gas varies inversely as the pressure to which it is subjected. In other words, if pressure is brought to bear on a known volume of gas, this volume will decrease as the pressure increases. This law may also be expressed as a proportion:

$$\frac{V}{V'}=\frac{P'}{P}$$

in which V = original volume;
V' = new volume;
P' = new pressure;
P = original pressure.

EXAMPLE 1.—What volume will 500 liters of a gas, under a pressure of 770 millimeters, occupy under a pressure of 700 millimeters?

SOLUTION.—From the proportion, we get

$$V'P'=VP$$

$$V'=\frac{VP}{P'}$$

$$V'=\frac{500\times 770}{700}=550 \text{ liters of oxygen}$$

EXAMPLE 2.—A certain quantity of air occupies 1,000 cubic centimeters under a pressure of 720 millimeters. What volume will it occupy if the pressure is increased to 780 millimeters?

SOLUTION.—By substitution,

$$V'=\frac{VP}{P'}$$

$$V'=\frac{1{,}000\times 720}{780}=923.08 \text{ cubic centimeters}$$

Case IV.—Sometimes it becomes necessary to correct the volume of a gas for both temperature and pressure at the same time. This can, of course, be performed by correcting the volume for one factor, and then by using the corrected volume as the starting point, for the other factor. By combining the two formulas for the correction of volume, the same end can be reached by one operation by means of the following formula:

$$V'=\frac{T'PV}{TP'}$$

in which V' = new volume;
V = original volume;
T' = new absolute temperature $(273+t)$;
T = original absolute temperature $(273+t)$;
P' = new pressure;
P = original pressure.

The following examples show applications of this formula:

EXAMPLE 1.—A gas occupies 100 liters at a temperature of 20° C. and under a pressure of 780 millimeters. What will its volume be at a temperature of −5° C. and under a pressure of 760 millimeters?

SOLUTION.—By the formula,

$$V' = \frac{(273-5)\times 780\times 100}{(273+20)\times 760} = 93.87 \text{ liters}$$

EXAMPLE 2.—How many liters will a mass of carbon dioxide gas occupy at 0° C. and 740 millimeters if it has a volume of 20 liters at 40° C. and 780 millimeters?

SOLUTION.—By the formula,

$$V' = \frac{273\times 780\times 20}{(273+40)\times 740} = 18.37 \text{ liters}$$

22. Solution of Problems Involving Weights and Gaseous Volumes.—In chemical work, one is sometimes required to determine how much, by weight, of a substance is needed to produce a certain volume of a gas under definite conditions of temperature and pressure; or how much, by volume, of a gas under certain conditions of temperature and pressure is formed when definite amounts of substances are chemically combined. These determinations are based on reduction of the volumes of the gases under various conditions of temperature to the volume at 0° C. and 760 millimeters, and then on changing to the weight equivalents by using the rule that the weight of 1 liter of a gas is equal to its density multiplied by the weight of 1 liter of hydrogen at 0° C. and 760 millimeters, or vice versa.

The following examples show how problems involving both weights and volumes are solved:

EXAMPLE 1.—If 200 grams of mercuric oxide, HgO, are decomposed into mercury and oxygen, how many liters of oxygen at a temperature of 50° C. and a pressure of 790 millimeters will be obtained?

SOLUTION.—Write the equation representing the reaction,

$$\underset{200}{\overset{433.2}{2HgO}} = 2Hg + \underset{x}{\overset{32}{O_2}}$$

$$\frac{433.2}{200} = \frac{32}{x}$$

$$433.2x = 32 \times 200$$

$$x = \frac{32 \times 200}{433.2} = 14.77 \text{ grams of oxygen}$$

1 liter of oxygen weighs $16 \times .089873 = 1.44$ grams.

Then, $14.77 \text{ grams} = 14.77 \div 1.44 = 10.25$ liters of oxygen

$$V' = \frac{(273+50) \times 760 \times 10.25}{273 \times 790} = 11.67 \text{ liters}$$

This problem is a calculation in which a conversion of weight to volume is involved. In problems of this type, it is first necessary to calculate the weight of the substance, the volume of which is required; second, to convert the weight to its equivalent volume at 0° C. and 760 millimeters (expressed in liters); third, to change this volume to the volume at the required temperature and pressure.

The following example is a calculation involving a conversion from volume to weight:

EXAMPLE 2.—In order to prepare 10 liters of hydrogen at 40° C. and 720 millimeters by the action of sulphuric acid on zinc, how much zinc must be used?

SOLUTION.—The first step is to reduce the volume of the gas, 10 liters, at 40° C. and 720 millimeters to the volume which the gas would occupy at 0° C. and 760 millimeters.

$$V' \frac{273 \times 720 \times 10}{(273+40) \times 760} = 8.26 \text{ liters of hydrogen}$$

The second step is to determine the weight of 8.26 liters of hydrogen. One liter weighs .089873 gram, 8.26 liters weigh $8.26 \times .089873 = .7423$ gram. Now write the equation representing the reaction.

$$\underset{x}{\overset{65.37}{Zn}} + H_2SO_4 = ZnSO_4 + \underset{.7423}{\overset{2.016}{H_2}}$$

$$\frac{65.37}{x} = \frac{2.016}{.7423}$$

$$2.016x = 65.37 \times .7423$$

$$x = \frac{65.37 \times .7423}{2.016} = 24.06 \text{ grams of zinc}$$

This problem, involving a conversion from volume to weight, includes several definite steps. First, the volume of the gas required is changed to its volume at 0° C. and 760 millimeters; second, the volume at 0° C. and 760 millimeters is converted to its weight equivalent in grams; third, the weight of gas needed is used as a basis for calculating the weights of substances needed to produce the required volume of gas.

23. The best method by which a student may become familiar with the solution of chemical problems is to solve all kinds in such a way that every step will be clearly understood and that problems of like nature will be recognized when met in industrial work. Following are examples for practice that will serve to meet these requirements if the student carefully solves each of them so that he gets the correct answer and knows why he performed each step in the calculation.

EXAMPLES FOR PRACTICE

1. Calculate the percentage composition of potassium acid sulphate, $KHSO_4$.

$$\text{Ans.}\begin{cases} K = 28.714\% \\ H = 0.740\% \\ S = 23.544\% \\ O = 47.000\% \end{cases}$$

2. Calculate the percentage composition of calcium chloride, $CaCl_2$.

$$\text{Ans.}\begin{cases} Ca = 36.103\% \\ Cl = 63.897\% \end{cases}$$

3. Calculate the percentage composition of borax, $Na_2B_4O_7$.

$$\text{Ans.}\begin{cases} Na = 22.82\% \\ B = 21.62\% \\ O = 55.55\% \end{cases}$$

4. What quantity of lime, CaO, can be obtained from 1,000 pounds of calcium carbonate, $CaCO_3$? Ans. 560.28 lb.

5. How much arsenious oxide, As_2O_3, may be obtained from 100 pounds of magnesium pyroarsenate, $Mg_2As_2O_7$? Ans. 63.73 lb.

6. What percentage of sulphur trioxide, SO_3, is contained in barium sulphate, $BaSO_4$? Ans. 34.2%

7. Zinc chloride, $ZnCl_2$, may be made by treating zinc oxide, ZnO, with hydrochloric acid, HCl. The reaction is represented by the following equation:

$$ZnO + 2HCl = ZnCl_2 + H_2O$$

(*a*) How much ZnO will react with 100 kilograms of HCl?
(*b*) How much HCl will be necessary to make 150 kilograms of $ZnCl_2$?

Ans. $\begin{cases} (a) & 111.56 \text{ kg.} \\ (b) & 80.27 \text{ kg.} \end{cases}$

8. The reaction between ammonium chloride, NH_4Cl, and lime, CaO, may be represented by the equation,

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$$

How much lime will be required to make 30 pounds of ammonia, NH_3?
Ans. 49.38 lb.

9. A compound has the following composition: Silver, 70.13%; oxygen, 20.77%; and nitrogen, 9.09%. Calculate its formula from these figures. Ans. $AgNO_2$

10. A compound contains 43.4% sodium, 11.32% carbon, and 45.28% oxygen What is its formula? Ans. Na_2CO_3

11. The approximate density of oxygen is 16. What is the weight of 100 liters of oxygen at 0° C. and 760 millimeters? Ans. 143.7968 grams

12. The approximate density of hydrogen sulphide, H_2S, is 17. What is the weight of 10 liters of the gas at 0° C. and 760 millimeters?
Ans. 15.278 grams

13. What is the weight of 50 liters of nitrogen at 0° C. and 760 millimeters, the approximate density of nitrogen being 14? Ans. 62.911 grams

14. Calculate the volume in liters of 250 grams of oxygen at 0° C. and 760 millimeters. Ans. 173.75 liters

15. Hydrogen is formed by the action of sulphuric acid on zinc; thus,

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

(*a*) What amount of $ZnSO_4$ is formed when 15 grams of zinc are treated with sulphuric acid? Ans. 37.04 grams

(*b*) How much zinc is required to form zinc sulphate with 20 grams of sulphuric acid? Ans. 13.33 grams

(*c*) How many liters of hydrogen are formed at 0° C. and 760 millimeters pressure when 45 grams of zinc are treated with sulphuric acid?
Ans. 15.35 liters

(*d*) What volume of hydrogen is formed in (*c*) at 12° C. and 754 millimeters pressure? Ans. 16.15 liters

16. A gas occupies a volume of 500 liters at 30° C. and 760 millimeters. What volume will it occupy if the temperature and pressure are changed to 20° C. and 720 millimeters? Ans. 510.35 liters

17. Nitrogen (approximate density 14) occupies a volume of 100 liters at 50° C. and 780 millimeters. What is the weight of this mass of nitrogen?
Ans. 109.138 grams

RELATION OF SPECIFIC GRAVITY TO DEGREES BAUMÉ

24. As the strength of all the common mineral acids, such as, sulphuric, nitric, and hydrochloric, and solutions of some alkalies, are designated by their specific gravities (sp. gr.) or by degrees Baumé (° Bé.), it is important that one should know the relation existing between these values and be familiar with the rapid practical methods by which each is obtained.

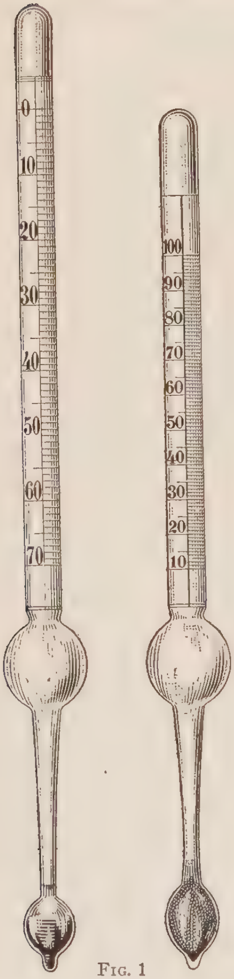


Fig. 1

25. The specific gravity of a solution, according to a previous definition, is the weight of a volume of the solution compared with the weight of an equal volume of water at the same temperature. For instance, the specific gravity of ordinary C. P. (chemically pure) sulphuric acid is 1.84, which may be interpreted to mean that a volume of this acid is 1.84 times as heavy as an equal volume of water at the same temperature. In other words, the weight of 1 cubic centimeter of the acid, at 15° C., may be taken as 1.84 grams. Therefore, instead of weighing out the acid which may be called for in an experiment, approximate weights may be obtained by measuring out the volume corresponding to this weight.

Example.—The directions for a certain experiment call for 100 grams C. P. sulphuric acid, specific gravity (sp. gr.), 1.84. How may this weight of acid be approximately obtained in the event that a balance is not available?

Solution.—Since one cubic centimeter (1 cc.), weighs 1.84 grams, $100 \div 1.84 = 54.3$ cubic centimeters, the volume of this acid corresponding to 100 grams.

26. One form of instrument commonly used for determining degrees Baumé is called a **hydrometer,** which is illustrated in Fig. 1. This instrument is usually made of glass and is weighted at one end so that it will float in a liquid in a vertical position.

Several types of hydrometers are in use, each designed for a special purpose, but the Baumé hydrometer, which is generally used, is the only one which need be described. Of this type of hydrometer, two kinds are used, one for liquids lighter than water (shown at the right in the illustration) and the other for liquids heavier than water (shown at the left in the illustration). When the first is placed in pure water at 15.6° C. or 60° F., it floats so that the surface of the water and the graduation on its stem, marked 10, coincide with the surface of the water, while the second kind sinks in the water until the surface of the latter is at the graduation marked 0.

To use either a hydrometer showing specific gravities, or the Baumé hydrometer, the instrument is placed in a cylinder containing the liquid at the proper temperature, usually 15.56° C. or 60° F., in commercial types, and specific gravity or degrees Baumé are read directly from the stem at the surface of the liquid.

CALCULATION OF DEGREES BAUMÉ AND SPECIFIC GRAVITY

27. Conversion of degrees Baumé to specific gravity and specific gravity to degrees Baumé can be easily accomplished by the aid of the following formulas:

For Liquids Lighter Than Water

$$\text{Specific gravity} = \frac{140}{\text{degrees Baumé} + 130}$$

$$\text{Degrees Baumé} = \frac{140}{\text{specific gravity}} - 130$$

For Liquids Heavier Than Water

$$\text{Specific gravity} = \frac{145}{145 - \text{degrees Baumé}}$$

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{specific gravity}}$$

TABLE II*

DEGREES BAUMÉ CORRESPONDING TO SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F. $\left(\frac{15°.56}{15°.56}\text{ C.}\right)$ FOR LIQUIDS HEAVIER THAN WATER

Sp. Gr. $\frac{15°.56}{15°.56}$ Cent.	0	1	2	3	4	5	6	7	8	9
1.00	0.000	0.145	0.289	0.434	0.578	0.721	0.865	1.008	1.151	1.293
1.01	1.436	1.578	1.719	1.816	2.002	2.143	2.283	2.424	2.564	2.704
1.02	2.843	2.982	3.121	3.260	3.399	3.537	3.675	3.812	3.950	4.087
1.03	4 223	4.360	4.496	4.632	4.768	4.903	5.038	5.174	5.308	5.443
1.04	5.577	5.711	5.845	5.978	6.111	6.244	6.377	6.509	6.641	6.773
1.05	6.905	7.036	7.167	7.298	7.429	7.559	7.689	7.819	7.949	8.078
1.06	8.208	8.336	8.465	8.594	8.722	8.850	8.978	9.105	9.232	9.359
1.07	9.486	9.613	9.739	9.991	9.991	10.116	10.242	10.367	10.492	10.616
1.08	10.741	10.865	10.989	11.113	11.236	11.359	11.483	11.605	11.728	11.850
1.09	11.972	12.094	12.216	12.338	12.459	12.580	12.701	12.821	12.942	13.062
1.10	13.182	13.302	13.421	13.540	13.659	13.778	13.897	14.015	14.134	14.252
1.11	14.370	14.487	14.604	14.721	14.838	14.955	15.072	15.188	15.304	15.420
1.12	15.536	15.561	15.767	15.882	15.997	16.111	16.226	16.340	16.454	16.568
1.13	10.682	16.795	16.908	17.021	17.134	17.247	17.359	17.471	17.583	17.695
1.14	17.807	17.919	18.030	18.141	18.252	18.363	18.473	18.583	18.693	18.803
1.15	18.913	19.023	19.132	19.241	19.350	19.459	19.568	19.676	19.784	19.892
1.16	20.000	20.108	20.215	20.322	20.430	20.536	20.643	20.750	20.856	20.962
1.17	21.068	21.174	21.280	21.385	21.491	21.596	21.701	21.806	21.910	22.014
1.18	22.119	22.223	22.327	22.430	22.534	22.637	22.740	22.843	22.946	23.049
1.19	23.151	23.254	23.356	23.458	23.560	23.661	23.763	23.864	23.965	24.066
1.20	24.167	24.267	24.368	24.468	24.568	24.668	24.768	24.868	24.967	25.066
1.21	25.165	25.264	25.363	25.462	25.560	25.658	25.755	25.855	25.952	26.050
1.22	26.148	26.245	26.342	26.439	26.536	26.633	26.729	26.826	26.922	27.018
1.23	27.114	27.210	27.305	27.401	27.496	27.591	27.686	27.781	27.876	27.970
1.24	28.065	28.159	28.253	28.347	28.441	28.534	28.628	28.721	28.814	28.907
1.25	29.000	29.093	29.185	29.278	29.370	29.462	29.554	29.646	29.738	29.829
1.26	29.921	30.012	30.103	30.194	30.285	30.376	30.466	30.556	30.647	30.737
1.27	30.827	30.917	31.006	31.096	31.185	31.275	31.364	31.453	31.542	31.630
1.28	31.719	31.807	31.896	31.984	32.072	32.160	32.247	32.335	32.422	32.510
1.29	32.597	32.684	32.771	32.858	32.944	33.031	33.117	33.204	33.290	33.376
1.30	33.462	33.547	33.633	33.718	33.804	33.889	33.974	34.059	34.144	34.229
1.31	34.313	34.397	34.482	34.566	34.650	34.734	34.818	34.901	34.985	35.068
1.32	35.152	35.235	35.318	35.401	35.483	35.566	35.649	35.731	35.813	35.895
1.33	35.977	36.059	36.141	36.223	36.304	36.386	36.467	36.548	36.629	36.710
1.34	36.791	36.872	36.952	37.033	37.113	37.193	37.273	37.353	37.433	37.513
1.35	37.593	37.672	37.751	37.831	37.910	37.989	38.068	38.147	38.225	38.304
1.36	38.382	38.461	38.539	38.617	38.695	38.773	38.851	38.928	39.006	39.803
1.37	39.161	39.238	39.315	39.392	39.469	39.546	39.622	39.609	39.775	39.851
1.38	39.928	40.004	40.080	40.156	40.231	40.307	40.382	40.458	40.533	40.608
1.39	40.683	40.758	40.833	40.908	40.983	41.057	41.132	41.206	41.280	41.355
1.40	41.429	41.503	41.576	41.650	41.724	41.797	41.871	41.944	42.017	42.090
1.41	42.163	42.236	42.309	42.381	42.454	42.527	42.599	42.671	42.743	42.815
1.42	42.887	42.959	43.031	43.103	43.174	43.246	43.317	43.388	43.459	43.530
1.43	43.601	43.672	43.743	43.814	43.884	43.955	44.025	44.095	44.165	44.236
1.44	44.306	44.376	44.445	44.515	44.585	44.654	44.724	44.793	44.862	44.931
1.45	45.000	45.069	45.138	45.207	45.275	45.344	45.412	45.481	45.549	45.617

*Data obtained from Circular No. 19, Bureau of Standards.

TABLE II—(*Continued*)

DEGREES BAUMÉ CORRESPONDING TO SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F. $\left(\frac{15°.56}{15°.56}\text{ C.}\right)$ FOR LIQUIDS HEAVIER THAN WATER

Sp. Gr. $\frac{15°.56}{15°.56}$ Cent.	0	1	2	3	4	5	6	7	8	9
1.46	45.635	45.753	45.821	45.889	45.956	46.024	46.091	46.159	46.226	46.293
1.47	46.361	46.428	46.495	46.562	46.628	46.695	46.762	46.828	46.894	46.961
1.48	47.027	47.093	47.159	47.225	47.291	47.357	47.423	47.488	47.554	47.619
1.49	47.635	47.750	47.815	47.880	47.945	48.010	48.075	48.140	48.204	48.269
1.50	48.333	48.398	48.462	48.526	48.591	48.655	48.719	48.782	48.846	48.910
1.51	48.974	49.037	49.101	49.164	49.227	49.290	49.354	49.417	49.480	49.543
1.52	49.605	49.668	49.731	49.793	49.856	49.918	49.980	50.043	50.105	50.167
1.53	50.229	50.291	50.353	50.414	50.476	50.538	50.599	50.660	50.722	50.783
1.54	50.844	50.905	50.966	51.027	51.088	51.149	51.210	51.270	51.331	51.391
1.55	51.452	51.512	51.572	51.632	51.692	51.752	51.812	51.872	51.932	51.992
1.56	52.051	52.111	52.170	52.230	52.289	52.348	52.407	52.467	52.526	52.585
1.57	52.643	52.702	52.761	52.820	52.878	52.937	52.995	53.053	53.112	53.170
1.58	53.228	53.286	53.344	53.402	53.460	53.517	53.575	53.633	53.690	53.748
1.59	53.805	53.862	53.920	53.977	54.034	54.091	54.148	54.205	54.262	54.318
1.60	54.375	54.432	54.488	54.545	54.601	54.657	54.714	54.770	54.826	54.882
1.61	54.938	54.994	55.050	55.106	55.161	55.217	55.272	55.328	55.383	55.439
1.62	55.494	55.549	55.604	55.659	55.714	55.769	55.824	55.879	55.934	55.988
1.63	56.043	56.098	56.152	56.206	56.261	56.315	56.369	56.423	56.478	56.531
1.64	56.585	56.639	56.693	56.747	56.801	56.854	56.908	56.961	57.015	57.068
1.65	57.121	57.175	57.228	57.281	57.334	57.387	57.440	57.493	57.545	57.598
1.66	57.651	57.703	57.756	57.808	57.861	57.913	57.965	58.017	58.070	58.122
1.67	58.174	58.226	58.278	58.329	58.381	58.433	58.485	58.536	58.588	58.639
1.68	58.690	58.742	58.793	58.844	58.896	58.947	58.998	59.049	59.100	59.150
1.69	59.201	59.252	59.303	59.353	59.404	59.454	59.505	59.555	59.605	59.656
1.70	59.706	59.756	59.806	59.856	59.906	59.956	60.006	60.056	60.105	60.155
1.71	60.205	60.254	60.304	60.353	60.403	60.452	60.501	60.550	60.600	60.649
1.72	60.698	60.747	60.796	60.844	60.893	60.942	60.991	61.039	61.088	61.136
1.73	61.185	61.234	61.282	61.330	61.378	61.427	61.475	61.523	61.571	61.619
1.74	61.667	61.715	61.762	61.810	61.858	61.906	61.953	62.001	62.048	62.096
1.75	62.143	62.190	62.237	62.285	62.332	62.379	62.426	62.473	62.520	62.567
1.76	62.614	62.660	62.707	62.754	62.801	62.847	62.894	62.940	62.987	63.033
1.77	63.079	63.125	63.172	63.218	63.264	63.310	63.356	63.402	63.448	63.494
1.78	63.539	63.585	63.631	63.676	63.722	63.768	63.813	63.858	63.904	63.949
1.79	63.994	64.040	64.085	64.130	64.175	64.220	64.265	64.310	64.355	64.400
1.80	64.445	64.489	64.534	64.579	64.623	64.668	64.712	64.575	64.801	64.845
1.81	64.890	64.934	64.978	65.022	65.066	65.110	65.154	65.198	65.242	65.286
1.82	65.330	65.374	65.417	65.461	65.504	65.548	65.591	65.635	65.678	65.722
1.83	65.765	65.808	65.852	65.895	65.938	65.981	66.024	66.067	66.110	66.153
1.84	66.196	66.238	66.281	66.324	66.367	66.409	66.452	66.494	66.537	66.579
1.85	66.622									

TABLE III

SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F. $\left(\frac{15°.56}{15°.56} \text{C.}\right)$ CORRESPONDING TO DEGREES BAUMÉ FOR LIQUIDS HEAVIER THAN WATER

Degrees Baumé	Tenths of Degrees Baumé									
	0	1	2	3	4	5	6	7	8	9
0	1.0000	1.0007	1.0014	1.0021	1.0028	1.0035	1.0042	1.0049	1.0055	1.0062
1	1.0069	1.0076	1.0083	1.0090	1.0097	1.0105	1.0112	1.0119	1.0126	1.0133
2	1.0140	1.0147	1.0154	1.0161	1.0168	1.0175	1.0183	1.0190	1.0197	1.0204
3	1.0211	1.0218	1.0226	1.0233	1.0240	1.0247	1.0255	1.0262	1.0269	1.0276
4	1.0284	1.0291	1.0298	1.0306	1.0313	1.0320	1.0328	1.0335	1.0342	1.0350
5	1.0357	1.0365	1.0372	1.0379	1.0387	1.0394	1.0402	1.0409	1.0417	1.0424
6	1.0432	1.0439	1.0447	1.0454	1.0462	1.0469	1.0477	1.0484	1.0492	1.0500
7	1.0507	1.0515	1.0522	1.0530	1.0538	1.0545	1.0553	1.0561	1.0569	1.0576
8	1.0584	1.0592	1.0599	1.0607	1.0615	1.0623	1.0630	1.0638	1.0646	1.0654
9	1.0662	1.0670	1.0677	1.0685	1.0693	1.0701	1.0709	1.0717	1.0725	1.0733
10	1.0741	1.0749	1.0757	1.0765	1.0773	1.0781	1.0789	1.0797	1.0805	1.0813
11	1.0821	1.0829	1.0837	1.0845	1.0853	1.0861	1.0870	1.0878	1.0886	1.0894
12	1.0902	1.0910	1.0919	1.0927	1.0935	1.0943	1.0952	1.0960	1.0968	1.0977
13	1.0985	1.0993	1.1002	1.1010	1.1018	1.1027	1.1035	1.1043	1.1052	1.1060
14	1.1069	1.1077	1.1086	1.1094	1.1103	1.1111	1.1120	1.1128	1.1137	1.1145
15	1.1154	1.1162	1.1171	1.1180	1.1188	1.1197	1.1206	1.1214	1.1223	1.1232
16	1.1240	1.1249	1.1258	1.1267	1.1275	1.1284	1.1293	1.1302	1.1310	1.1319
17	1.1328	1.1337	1.1346	1.1355	1.1364	1.1373	1.1381	1.1390	1.1399	1.1408
18	1.1417	1.1426	1.1435	1.1444	1.1453	1.1462	1.1472	1.1481	1.1490	1.1499
19	1.1508	1.1517	1.1526	1.1535	1.1545	1.1554	1.1563	1.1572	1.1581	1.1591
20	1.1600	1.1609	1.1619	1.1628	1.1637	1.1647	1.1656	1.1665	1.1675	1.1684
21	1.1694	1.1703	1.1712	1.1722	1.1731	1.1741	1.1750	1.1760	1.1769	1.1779
22	1.1789	1.1798	1.1808	1.1817	1.1827	1.1837	1.1846	1.1856	1.1866	1.1876
23	1.1885	1.1895	1.1905	1.1915	1.1924	1.1934	1.1944	1.1954	1.1964	1.1974
24	1.1983	1.1993	1.2003	1.2013	1.2023	1.2033	1.2043	1.2053	1.2063	1.2073
25	1.2083	1.2093	1.2104	1.2114	1.2124	1.2134	1.2144	1.2154	1.2164	1.2175
26	1.2185	1.2195	1.2205	1.2216	1.2226	1.2236	1.2247	1.2257	1.2267	1.2278
27	1.2288	1.2299	1.2309	1.2319	1.2330	1.2340	1.2351	1.2361	1.2372	1.2383
28	1.2393	1.2404	1.2414	1.2425	1.2436	1.2446	1.2457	1.2468	1.2478	1.2489
29	1.2500	1.2511	1.2522	1.2532	1.2543	1.2554	1.2565	1.2576	1.2587	1.2598
30	1.2609	1.2620	1.2631	1.2642	1.2653	1.2664	1.2675	1.2686	1.2697	1.2708
31	1.2719	1.2730	1.2742	1.2753	1.2764	1.2775	1.2787	1.2798	1.2809	1.2821
32	1.2832	1.2843	1.2855	1.2866	1.2877	1.2889	1.2900	1.2912	1.2923	1.2935
33	1.2946	1.2958	1.2970	1.2981	1.2993	1.3004	1.3016	1.3028	1.3040	1.3051
34	1.3063	1.3075	1.3087	1.3098	1.3110	1.3122	1.3134	1.3146	1.3158	1.3170
35	1.3182	1.3194	1.3206	1.3218	1.3230	1.3242	1.3254	1.3266	1.3278	1.3291
36	1.3303	1.3315	1.3327	1.3339	1.3352	1.3364	1.3376	1.3389	1.3401	1.3414
37	1.3426	1.3438	1.3451	1.3463	1.3476	1.3488	1.3501	1.3514	1.3526	1.3539
38	1.3551	1.3564	1.3577	1.3590	1.3602	1.3615	1.3628	1.3641	1.3653	1.3666
39	1.3679	1.3692	1.3705	1.3718	1.3731	1.3744	1.3757	1.3770	1.3783	1.3796
40	1.3810	1.3823	1.3836	1.3849	1.3862	1.3876	1.3889	1.3902	1.3916	1.3929
41	1.3942	1.3956	1.3969	1.3983	1.3996	1.4010	1.4023	1.4037	1.4050	1.4064
42	1.4078	1.4091	1.4105	1.4119	1.4133	1.4146	1.4160	1.4174	1.4188	1.4202
43	1.4216	1.4230	1.4244	1.4258	1.4272	1.4286	1.4300	1.4314	1.4328	1.4342
44	1.4356	1.4371	1.4385	1.4399	1.4414	1.4428	1.4442	1.4457	1.4471	1.4486
45	1.4500	1.4515	1.4529	1.4544	1.4558	1.4573	1.4588	1.4602	1.4617	1.4632
46	1.4646	1.4661	1.4676	1.4691	1.4706	1.4721	1.4736	1.4751	1.4766	1.4781
47	1.4796	1.4811	1.4826	1.4841	1.4857	1.4872	1.4887	1.4902	1.4918	1.4933
48	1.4948	1.4964	1.4979	1.4995	1.5010	1.5026	1.5041	1.5057	1.5073	1.5088
49	1.5104	1.5120	1.5136	1.5152	1.5167	1.5183	1.5199	1.5215	1.5231	1.5247
50	1.5263	1.5279	1.5295	1.5312	1.5328	1.5344	1.5360	1.5376	1.5393	1.5409
51	1.5426	1.5442	1.5458	1.5475	1.5491	1.5508	1.5525	1.5541	1.5558	1.5575
52	1.5591	z.5608	1.5625	1.5642	1.5659	1.5676	1.5693	1.5710	1.5727	1.5744
53	1.5761	1.5778	1.5795	1.5812	1.5830	1.5847	1.5864	1.5882	1.5899	1.5917
54	1.5934	1.5952	1.5969	1.5987	1.6004	1.6022	1.6040	1.6058	1.6075	1.6093
55	1.6111	1.6129	1.6147	1.6165	1.6183	1.6201	1.6219	1.6237	1.6256	1.6274
56	1.6292	1.6310	1.6329	1.6347	1.6366	1.6384	1.6403	1.6421	1.6440	1.6459
57	1.6477	1.6496	1.6515	1.6534	1.6553	1.6571	1.6590	1.6609	1.6628	1.6648
58	1.6667	1.6686	1.6705	1.6724	1.6744	1.6763	1.6782	1.6802	1.6821	1.6841
59	1.6860	1.6880	1.6900	1.6919	1.6939	1.6959	1.6979	1.6999	1.7019	1.7039
60	1.7059	1.7079	1.7099	1.7119	1.7139	1.7160	1.7180	1.7200	1.7221	1.7241
61	1.7262	1.7282	1.7303	1.7324	1.7344	1.7365	1.7386	1.7407	1.7428	1.7449
62	1.7470	1.7491	1.7512	1.7533	1.7554	1.7576	1.7597	1.7618	1.7640	1.7661
63	1.7683	1.7705	1.7726	1.7748	1.7770	1.7791	1.7813	1.7835	1.7857	1.7879
64	1.7901	1.7923	1.7946	1.7968	1.7990	1.8012	1.8035	1.8057	1.8080	1.8102
65	1.8125	1.8148	1.8170	1.8193	1.8216	1.8239	1.8262	1.8285	1.8308	1.8331
66	1.8354	1.8378	1.8401	1.8424	1.8448	1.8471	1.8495	1.8519	1.8542	1.8566
67	1.8590	1.8614	1.8638	1.8662	1.8686	1.8710	1.8734	1.8758	1.8782	1.8807
68	1.8831	1.8856	1.8880	1.8905	1.8930	1.8954	1.8979	1.9004	1.9029	1.9054
69	1.9079	1.9104	1.9129	1.9155	1.9180	1.9205	1.9231	1.9256	1.9282	1.9308
70	1.9333									

TABLE IV

DEGREES BAUMÉ CORRESPONDING TO SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F. $\left(\frac{15°.56}{15°.56}\text{ C.}\right)$ FOR LIQUIDS LIGHTER THAN WATER

Sp. Gr. $\frac{15°.56}{15°.56}$ Cent.	0	1	2	3	4	5	6	7	8	9
0.60	103.333	102.945	102.558	102.172	101.788	101.405	101.023	100.642	100.263	99.885
.61	99.508	99.133	98.758	98.385	98.013	97.642	97.273	96.904	96.537	96.171
.62	95.806	95.443	95.080	94.719	94.359	94.000	93.642	93.285	92.930	92.576
.63	92.222	91.870	91.519	91.169	90.820	90.472	90.126	89.780	89.436	89.092
.64	88.750	88.409	88.068	87.729	87.391	87.054	86.718	86.383	86.049	85.716
.65	85.385	85.054	84.724	84.395	84.067	83.741	83.415	83.090	82.766	82.443
.66	82.121	81.800	81.480	81.161	80.843	80.526	80.210	79.895	79.581	79.268
.67	78.955	78.644	78.333	78.024	77.715	77.407	77.101	76.795	76.490	76.186
.68	75.882	75.580	75.279	74.978	74.678	74.380	74.082	73.785	73.488	73.193
.69	72.899	72.605	72.312	72.020	71.729	71.439	71.149	70.861	70.573	70.286
.70	70.000	69.715	69.430	69.146	68.864	68.582	68.300	68.020	67.740	67.461
.71	67.183	66.906	66.629	66.354	66.078	65.804	65.531	65.258	64.986	64.715
.72	64.444	64.175	63.906	63.638	63.370	63.103	62.837	62.572	62.308	62.044
.73	61.781	61.518	61.257	60.996	60.736	60.476	60.217	59.959	59.702	59.445
.74	59.189	58.934	58.679	58.425	58.172	57.919	57.668	57.416	57.166	56.916
.75	56.667	56.418	56.170	55.923	55.676	55.430	55.185	54.941	54.697	54.453
.76	54.210	53.968	53.727	53.486	53.246	53.007	52.768	52.529	52.292	52.055
.77	51.818	51.582	51.347	51.113	50.879	50.645	50.412	50.180	49.949	49.718
.78	49.487	49.257	49.028	48.799	48.571	48.344	48.117	47.891	47.665	47.440
.79	47.215	46.991	46.768	46.545	46.322	46.101	45.879	45.659	45.439	45.219
.80	45.000	44.781	44.564	44.346	44.129	43.913	43.697	43.482	43.267	43.053
.81	42.840	42.626	42.414	42.202	41.990	41.779	41.569	41.359	41.149	40.940
.82	40.732	40.524	40.316	40.109	39.903	39.697	39.492	39.287	39.082	38.878
.83	38.675	38.472	38.269	38.067	37.866	37.665	37.464	37.264	37.064	36.866
.34	36.667	36.469	36.271	36.074	35.877	35.680	35.485	35.289	35.094	34.900
.85	34.706	34.512	34.319	34.127	33.934	33.743	33.551	33.361	33.170	32.980
.86	32.791	32.602	32.413	32.225	32.037	31.850	31.663	31.476	31.290	31.105
.87	30.920	30.735	30.550	30.366	30.183	30.000	29.817	29.635	29.453	29.272
.88	29.091	28.910	28.730	28.550	28.371	28.192	28.014	27.835	27.658	27.480
.89	27.303	27.127	26.951	26.775	26.600	26.425	26.250	26.076	25.902	25.729
.90	25.556	25.383	25.211	25.039	24.867	24.696	24.525	24.355	24.185	24.015
.91	23.846	23.677	23.509	23.341	23.173	23.005	22.838	22.672	22.506	22.339
.92	22.174	22.009	21.844	21.679	21.515	21.351	21.188	21.025	20.862	20.700
.93	20.538	20.376	20.215	20.054	19.893	19.733	19.573	19.413	19.254	19.095
.94	18.936	18.778	18.620	18.462	18.305	18.148	17.991	17.835	17.679	17.524
.95	17.368	17.214	17.059	16.905	16.751	16.597	16.444	16.290	16.138	15.985
.96	15.833	15.682	15.530	15.379	15.228	15.078	14.928	14.778	14.628	14.479
.97	14.330	14.181	14.033	13.885	13.737	13.590	13.443	13.297	13.149	13.003
.98	12.857	12.712	12.566	12.421	12.276	12.132	11.988	11.844	11.700	11.557
.99	11.414	11.271	11.129	10.987	10.845	10.704	10.562	10.421	10.281	10.140
1.00	10.000									

TABLE V

SPECIFIC GRAVITIES AT $\frac{60^\circ}{60^\circ}$ F. $\left(\frac{15^\circ.56}{15^\circ.56}\text{ C.}\right)$ CORRESPONDING TO DEGREES BAUMÉ FOR LIQUIDS LIGHTER THAN WATER

Degrees Baumé	Tenths of Degrees Baumé									
	0	1	2	3	4	5	6	7	8	9
10	1.0000	0.9993	0.9986	0.9979	0.9972	0.9964	0.9957	0.9950	0.9943	0.9936
11	.9929	.9922	.9915	.9908	.9901	.9894	.9887	.9880	.9873	.9866
12	.9859	.9852	.9845	.9838	.9831	.9825	.9818	.9811	.9804	.9797
13	.9790	.9783	.9777	.9770	.9763	.9756	.9749	.9743	.9736	.9729
14	.9722	.9715	.9709	.9702	.9695	.9689	.9682	.9675	.9669	.9662
15	.9655	.9649	.9642	.9635	.9629	.9622	.9615	.9609	.9602	.9596
16	.9589	.9582	.9576	.9569	.9563	.9556	.9550	.9543	.9537	.9530
17	.9524	.9517	.9511	.9504	.9498	.9492	.9485	.9479	.9472	.9466
18	.9459	.9453	.9447	.9440	.9434	.9428	.9421	.9415	.9409	.9402
19	.9396	.9390	.9383	.9377	.9371	.9365	.9358	.9352	.9346	.9340
20	.9333	.9327	.9321	.9315	.9309	.9302	.9296	.9290	.9284	.9278
21	.9272	.9265	.9259	.9253	.9247	.9241	.9235	.9229	.9223	.9217
22	.9211	.9204	.9198	.9192	.9186	.9180	.9174	.9168	.9162	.9156
23	.9150	.9144	.9138	.9132	.9126	.9121	.9115	.9109	.9103	.9097
24	.9091	.9085	.9079	.9073	.9067	.9061	.9056	.9050	.9044	.9038
25	.9032	.9026	.9021	.9015	.9009	.9003	.8997	.8992	.8986	.8980
26	.8974	.8969	.8963	.8957	.8951	.8946	.8940	.8934	.8929	.8923
27	.8917	.8912	.8906	.8900	.8895	.8889	.8883	.8878	.8872	.8866
28	.8861	.8855	.8850	.8844	.8838	.8833	.8827	.8822	.8816	.8811
29	.8805	.8799	.8794	.8788	.8783	.8777	.8772	.8766	.8761	.8755
30	.8750	.8745	.8739	.8734	.8728	.8723	.8717	.8712	.8706	.8701
31	.8696	.8690	.8685	.8679	.8674	.8669	.8663	.8658	.8653	.8647
32	.8642	.8637	.8631	.8626	.8621	.8615	.8610	.8605	.8600	.8594
33	.8589	.8584	.8578	.8573	.8568	.8563	.8557	.8552	.8547	.8542
34	.8537	.8531	.8526	.8521	.8516	.8511	.8505	.8500	.8495	.8490
35	.8485	.8480	.8475	.8469	.8464	.8459	.8454	.8449	.8444	.8439
36	.8434	.8429	.8424	.8419	.8413	.8408	.8403	.8398	.8393	.8388
37	.8383	.8378	.8373	.8368	.8363	.8358	.8353	.8348	.8343	.8338
38	.8333	.8328	.8323	.8318	.8314	.8309	.8304	.8299	.8294	.8289
39	.8284	.8279	.8274	.8269	.8264	.8260	.8255	.8250	.8245	.8240
40	.8235	.8230	.8226	.8221	.8216	.8211	.8206	.8202	.8197	.8192
41	.8187	.8182	.8178	.8173	.8168	.8163	.8159	.8154	.8149	.8144
42	.8140	.8135	.8130	.8125	.8121	.8116	.8111	.8107	.8102	.8097
43	.8092	.8088	.8083	.8078	.8074	.8069	.8065	.8060	.8055	.8051
44	.8046	.8041	.8037	.8032	.8028	.8023	.8018	.8014	.8009	.8005
45	.8000	.7995	.7991	.7986	.7982	.7977	.7973	.7968	.7964	.7959
46	.7955	.7950	.7946	.7941	.7937	.7932	.7928	.7923	.7919	.7914
47	.7910	.7905	.7901	.7896	.7892	.7887	.7883	.7878	.7874	.7870
48	.7865	.7861	.7856	.7852	.7848	.7843	.7839	.7834	.7830	.7826
49	.7821	.7817	.7812	.7808	.7804	.7799	.7795	.7791	.7786	.7782
50	.7778	.7773	.7769	.7765	.7761	.7756	.7752	.7748	.7743	.7739
51	.7735	.7731	.7726	.7722	.7718	.7713	.7709	.7705	.7701	.7697
52	.7692	.7688	.7684	.7680	.7675	.7671	.7667	.7663	.7659	.7654
53	.7650	.7646	.7642	.7638	.7634	.7629	.7625	.7621	.7617	.7613
54	.7609	.7605	.7600	.7596	.7592	.7588	.7584	.7580	.7576	.7572

TABLE V—(*Continued*)

SPECIFIC GRAVITIES AT $\frac{60°}{60°}$ F. $\left(\frac{15°.56}{15°.56}\text{ C.}\right)$ CORRESPONDING TO DEGREES BAUMÉ FOR LIQUIDS LIGHTER THAN WATER

Degrees Baumé	Tenths of Degrees Baumé									
	0	1	2	3	4	5	6	7	8	9
55	0.7568	0.7563	0.7559	0.7555	0.7551	0.7547	0.7543	0.7539	0.7535	0.7531
56	.7527	.7523	.7519	.7515	.7511	.7507	.7503	.7499	.7495	.7491
57	.7487	.7483	.7479	.7475	.7471	.7467	.7463	.7459	.7455	.7451
58	.7447	.7443	.7439	.7435	.7431	.7427	.7423	.7419	.7415	.7411
59	.7407	.7403	.7400	.7396	.7392	.7388	.7384	.7380	.7376	.7372
60	.7368	.7365	.7361	.7357	.7353	.7349	.7345	.7341	.7338	.7334
61	.7330	.7326	.7322	.7318	.7315	.7311	.7307	.7303	.7299	.7295
62	.7292	.7288	.7284	.7280	.7277	.7273	.7269	.7265	.7261	.7258
63	.7254	.7250	.7246	.7243	.7239	.7235	.7231	.7228	.7224	.7220
64	.7216	.7213	.7209	.7205	.7202	.7198	.7194	.7191	.7187	.7183
65	.7179	.7176	.7172	.7168	.7165	.7161	.7157	.7154	.7150	.7147
66	.7143	.7139	.7136	.7132	.7128	.7125	.7121	.7117	.7114	.7110
67	.7107	.7103	.7099	.7096	.7092	.7089	.7085	.7081	.7078	.7074
68	.7071	.7067	.7064	.7060	.7056	.7053	.7049	.7046	.7042	.7039
69	.7035	.7032	.7028	.7025	.7021	.7018	.7014	.7011	.7007	.7004
70	.7000	.6997	.6993	.6990	.6986	.6983	.6979	.6976	.6972	.6969
71	.6965	.6962	.6958	.6955	.6951	.6948	.6944	.6941	.6938	.6934
72	.6931	.6927	.6924	.6920	.6917	.6914	.6910	.6907	.6903	.6900
73	.6897	.6893	.6890	.6886	.6883	.6880	.6876	.6873	.6869	.6866
74	.6863	.6859	.6856	.6853	.6849	.6846	.6843	.6839	.6836	.6833
75	.6829	.6826	.6823	.6819	.6816	.6813	.6809	.6806	.6803	.6799
76	.6796	.6793	.6790	.6786	.6783	.6780	.6776	.6773	.6770	.6767
77	.6763	.6760	.6757	.6753	.6750	.6747	.6744	.6740	.6737	.6734
78	.6731	.6728	.6724	.6721	.6718	.6715	.6711	.6708	.6705	.6702
79	.6699	.6695	.6692	.6689	.6686	.6683	.6679	.6676	.6673	.6670
80	.6667	.6663	.6660	.6657	.6654	.6651	.6648	.6645	.6641	.6638
81	.6635	.6632	.6629	.6626	.6623	.6619	.6616	.6613	.6610	.6607
82	.6604	.6601	.6598	.6594	.6591	.6588	.6585	.6582	.6579	.6576
83	.6573	.6570	.6567	.6564	.6560	.6557	.6554	.6551	.6548	.6545
84	.6542	.6539	.6536	.6533	.6530	.6527	.6524	.6521	.6518	.6515
85	.6512	.6509	.6506	.6503	.6500	.6497	.6494	.6490	.6487	.6484
86	.6482	.6479	.6476	.6473	.6470	.6467	.6464	.6461	.6458	.6455
87	.6452	.6449	.6446	.6443	.6440	.6437	.6434	.6431	.6428	.6425
88	.6422	.6419	.6416	.6413	.6410	.6407	.6404	.6401	.6399	.6396
89	.6393	.6390	.6387	.6384	.6381	.6378	.6375	.6372	.6369	.6367
90	.6364	.6361	.6358	.6355	.6352	.6349	.6346	.6343	.6341	.6338
91	.6335	.6332	.6329	.6326	.6323	.6321	.6318	.6315	.6312	.6309
92	.6306	.6303	.6301	.6298	.6295	.6292	.6289	.6286	.6284	.6281
93	.6278	.6275	.6272	.6270	.6267	.6264	.6261	.6258	.6256	.6253
94	.6250	.6247	.6244	.6242	.6239	.6236	.6233	.6231	.6228	.6225
95	.6222	.6219	.6217	.6214	.6211	.6208	.6206	.6203	.6200	.6197
96	.6195	.6192	.6189	.6186	.6184	.6181	.6178	.6176	.6173	.6170
97	.6167	.6165	.6162	.6159	.6157	.6154	.6151	.6148	.6146	.6143
98	.6140	.6138	.6135	.6132	.6130	.6127	.6124	.6122	.6119	.6116
99	.6114	.6111	.6108	.6106	.6103	.6100	.6098	.6095	.6092	.6090
100	.6087									

The specific gravity of a solution, whether of an acid, an alkali, or a salt, depends upon the per cent. of acid, alkali, or salt in solution, and in order to determine quickly the strength in per cent., of a certain solution, the foregoing tables based upon the results of actual analyses, have been published showing the relation existing between per cent., strength, specific gravity, and degrees Baumé, of frequently used chemicals such as mineral acids, and solutions of sodium hydroxide, potassium hydroxide, ferrous sulphate, and copper sulphate.

28. Explanation of Tables.—The expression $\frac{60°}{60°}$ F. or $\frac{15°.56}{15°.56}$ C. means that the specific gravity has been obtained by comparing the weight of the liquid at 60° F., or at 15°.56 C., with the weight of an equal volume of water at the same temperature. Frequently the temperature at which the specific gravity is taken is given as $\frac{20°}{4°}$ C., which means that the comparison of the weight of the liquid with the weight of an equal volume of water was made with the liquid at 20° C., and the water at 4° C.

In Table II, specific gravities are given in the first column on the left, beginning with 1.00. The third figure of the specific gravity is then obtained from the number heading each vertical column. To convert specific gravity into degrees Baumé, proceed as follows: Suppose that the specific gravity is 1.419; then the corresponding degrees Baumé will be found in column 9, in the horizontal line beginning with 1.41, and is 42.815. Thus, a specific gravity of 1.846 corresponds to 66.452° Bé., the last figure of the specific gravity being obtained from the column headed by the figure 6 and then by reading down column 6, until the horizontal line beginning with 1.84 is reached, when the figure 66.452 is obtained. The figures used for purposes of illustration are underlined in the table. Specific gravities are given to three decimal places in Table II, and in commercial work greater accuracy than this is seldom necessary.

In Table III 10° Bé. corresponds to a specific gravity of 1.0741, while 10.5° Bé. corresponds to a specific gravity of 1.0781, which is found at the point where column 5 meets the horizontal line beginning with 10° Bé. The figures are underlined in the table.

The explanations given for Tables II and III will suffice also for the use of Tables IV and V.

CRYSTALLOGRAPHY

29. Although crystallography is not properly a part of chemistry, some knowledge of this subject is of such importance to the chemist that it will be treated briefly at this point.

Most chemical substances when they pass from the liquid or gaseous into the solid state, assume some definite geometric form, or are said to crystallize. Crystals are produced when a substance such as potassium nitrate, is dissolved in water and the solution is allowed to evaporate gradually; when a body such as sulphur is melted and allowed to solidify by cooling; or when a volatile substance, such as iodine, is vaporized, and the vapor condensed on a cool surface.

When a solution will dissolve no more of the solid at a given temperature, the solution is saturated. If, however, the solution is boiled in a flask the solution will generally dissolve more of the solid and become supersaturated. If a small crystal of the solid is dropped into a supersaturated solution, crystallization will immediately begin and will continue until the point of saturation is reached.

Many native minerals exhibit perfect crystalline forms, though investigations have not yet disclosed the process of their formation. Judging from their perfect shape, the assumption is justified that the process of their formation must have been a necessarily slow one. Besides their regular shape, these crystalline bodies possess other remarkable properties, that is, a peculiar power of splitting in certain directions more readily than in others, a property that is known as cleavage; and in many cases they possess the property of allowing light

to pass more readily in certain directions than in others, giving rise to the well-known phenomena of double refraction.

A body assuming two distinct crystalline forms is said to be dimorphous; the study of even the more familiar elements

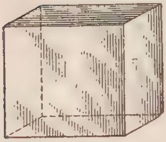


Fig. 2

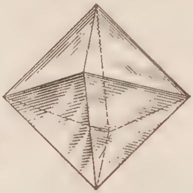


Fig. 3

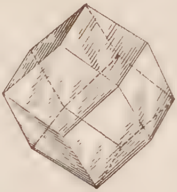


Fig. 4

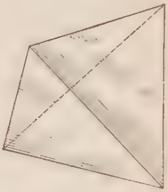


Fig. 5

includes some very important instances of dimorphism. A body that does not occur in crystals is termed amorphous; that is, without crystalline form. Certain complicated structures of the vegetable and animal world exhibit a structure that, although non-crystalline, is not devoid of a certain definite arrangement, and to which the name organized, or cellular, structure, has been given. A substance, however, may have both a crystalline and an amorphous variety.

As a rule, every particular substance possesses a definite form, in which it will always crystallize, and by which it may be distinguished; when a crystal is formed from aqueous solution, for instance, the most minute particle possesses the same crystalline structure and perfect form as the largest crystals.

Certain substances exhibiting a similarity in their chemical

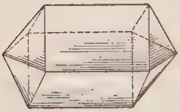


Fig. 6

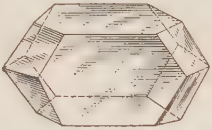


Fig. 7

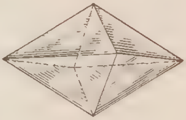


Fig. 8

constitution are found to crystallize in the same forms; these are said to be isomorphous.

30. Systems of Crystallization.—Many thousands of crystal forms are known, but they can all be referred to six classes or systems. This can be accomplished by comparing the crystals according to their directions of development.

1. *Regular or Isometric System.*—The simple forms of this system are the cube, Fig. 2; the regular octahedron, Fig. 3; the rhombic dodecahedron, Fig. 4; and the regular tetrahedron, Fig. 5.

The following are examples of substances crystallizing in this system: common salt, diamond, alum, iron pyrites, garnet, fluorspar, etc.

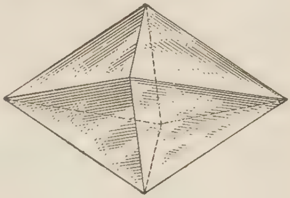


Fig. 9

2. *Quadratic* or *Tetragonal System.* The simple forms of this system are the first right square prism, Fig. 6; the second right square prism, Fig. 7; the first right square octahedron, Fig. 8; and the second right square octahedron, Fig. 9.

The following are examples of substances crystallizing in this system: stannic oxide, copper pyrites, yellow prussiate of potash, etc.

3. *Orthorhombic or Trimetric System.*—The chief forms of the crystals in this system are the right octahedron with

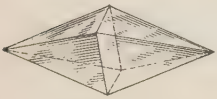


Fig. 10

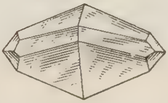


Fig. 11

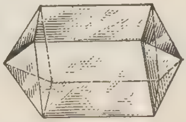


Fig. 12

rhombic base, Figs. 10 and 11, and the right rhombic prism, Fig. 12.

Examples of this class are: native sulphur, calcium sulphate, barium sulphate, magnesium sulphate, calcium carbonate, potassium nitrate, etc.

4. *Monoclinic, Monosymmetric, or Clinorhombic System.*

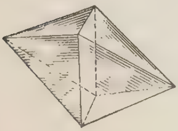


Fig. 13

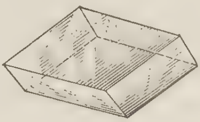


Fig. 14

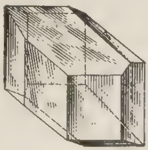


Fig. 15

The oblique rhombic octahedron, Fig. 13, belongs to this system.

Examples of this class are: sodium carbonate, sodium phosphate, borax, cane sugar, ferrous sulphate, etc.

5. *Triclinic, Asymmetric, or Clinorhomboidal System.*—The doubly oblique octahedron and the doubly oblique prism, Fig. 14, are the leading forms of this system. Copper sulphate, $CuSO_4{\cdot}5H_2O$, boric acid, the mineral albite, potassium bichromate, and a few other substances are found to crystallize in this system, the forms of which are generally very complicated. The crystalline form of copper sulphate is shown in Fig. 15.

6. *Hexagonal System.*—The hexagonal prism, Fig. 16, the

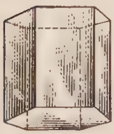


FIG. 16

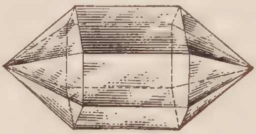


FIG. 17

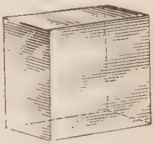


FIG. 18

regular six-sided pyramid, Fig. 17, and the rhombohedron, Fig. 18, are the common forms of the system.

Examples of this class are: graphite, mercuric sulphide, sodium nitrate, silicic oxide, calcium carbonate, ferrous carbonate, zinc carbonate, etc.

PERIODIC SYSTEM

31. It has long been known that certain remarkable numerical relations exist between the atomic weights of certain elements that are similar in their properties, and these elements are usually classed together as a group or family. For example, the elements lithium, sodium, and potassium are very similar in their properties and are usually classed together. If they are arranged in the order of their atomic weights, it will be seen that the atomic weight of one member is approximately the arithmetic mean of the atomic weights of those immediately before and after it, thus:

$$\begin{array}{ll} Li & 6.94 \\ Na & 23.00 \text{ and } \dfrac{6.94+39.1}{2}=23.02 \\ K & 39.10 \end{array}$$

Again, in the case of chlorine, bromine and iodine, we have:

$$\begin{array}{ll} Cl & 35.46 \\ Br & 79.92 \\ I & 126.92 \end{array} \text{ and } \frac{35.46+126.92}{2}=81.19$$

The same thing occurs in the case of sulphur, selenium, and tellurium:

$$\begin{array}{ll} S & 32.06 \\ Se & 79.20 \\ Te & 127.50 \end{array} \text{ and } \frac{32.06+127.5}{2}=79.78$$

By arranging the various groups of elements according to the difference between their atomic weights, it is also seen, that the increase in the atomic weights in each group takes place approximately by the same increment, for example:

F 19.00	*Na* 23.00	*Mg* 24.32
Difference = 16.46	Difference = 16.10	Difference = 15.75
Cl 35.46	*K* 39.10	*Ca* 40.07
Difference = 44.46	Difference = 46.35	Difference = 47.56
Br 79.92	*Rb* 85.45	*Sr* 87.63
Difference = 47.00	Difference = 47.36	Difference = 49.74
I 126.92	*Cs* 132.81	*Ba* 137.37

It should be noted that the first difference in each group is approximately 16, but the other differences are approximately three times this, or 48.

32. Newlands showed in 1864 that if the elements are arranged in the order of their increasing atomic weights, the properties belonging to each of the first seven elements reappear in the second seven. This relationship was further developed by Mendelejeff, and is known as the Periodic Law. In Table VI, the elements are tabulated on this basis, but owing to the recent discovery of the inert gases of the argon series, eight groups of elements have to be traversed before the properties of the first reappear. In this table, with the exception of hydrogen, the first sixteen elements with the lowest atomic weight are arranged in two rows of eight elements each, in the order of their increasing atomic weights, as follows:

He, 4.00	*Li*, 6.94	. . . . . .	*F*, 19.00
Ne, 20.20	*Na*, 23.00	. . . . . .	*Cl*, 35.46

etc.

33. The resemblance between the chemical and physical properties of the several members of each row, is at once apparent. Fluorine and chlorine, for example, are both corrosive gases, and are electronegative; lithium and sodium are both soft silver-white metals and are electropositive; while helium and neon have no such properties, being neither electropositive nor electronegative.

The several elements in any one row have equal powers of combining with oxygen, as here shown:

$$\begin{array}{ccccccc} Na_2O, & MgO, & Al_2O_3, & SiO_2, & P_2O_5, & SO_3, & Cl_2O_7 \\ & (Mg_2O_2) & & (Si_2O_4) & & (S_2O_6) & \end{array}$$

As regards combining with chlorine and hydrogen the valency of the elements in any one row is the same for each, a gradation in their combining powers being again seen, as follows:

$$\begin{array}{cccccccc} LiCl, & GlCl_2, & BCl_3, & CCl_4, & CH_4, & NH_3, & OH_2, & FH \\ NaCl, & MgCl_2, & (AlCl_3)_2, & SiCl_4, & SiH_4, & PH_3, & SH_2, & ClH \end{array}$$

The eight elements in the first row are know as a period, and their properties again appear in the various elements shown in the second row, which constitutes another period.

34. The properties of the compounds formed by the various elements also reappear, as for example, lithium chloride and sodium chloride, which are both similar; there is a similarity between glucinum oxide and magnesium oxide, and also between hydrofluoric and hydrochloric acids. As a result of the study of these relations existing between the elements, Mendelejeff stated the **periodic law** as follows:

The properties of the elements and their compounds form a periodic function of the atomic weights of the elements.

35. If the elements are arranged according to their increasing atomic weights, it will be seen from Table VI that, starting from argon and ending with bromine, eighteen elements occur before the properties of the first element reappear. This is known as a long period, as distinct from the two first periods, which are termed short periods. The first eight elements of a long period form the even series, the last seven elements the odd series, while the elements which come between the even

and the odd series of a long period, were called by Mendelejeff transitional elements and are placed in Group 8. In arranging the even and odd series of a long period, the elements are placed in such a way that the even and odd series appear in the table under the columns A and B, respectively.

The elements from krypton to iodine constitute another long period and it will be observed that a notable gap exists in the even series, corresponding to manganese in the first long period. Three more long periods follow, in which there are many gaps, probably indicating the existence of other elements which still remain to be discovered.

36. In the long periods the arrangement of the groups into subdivisions A and B shows the similarity in properties of the elements constituting each subdivision. For example, there are certain properties common to all the members of Group 2; at the same time, there is a much closer resemblance between calcium, barium, and strontium, than there is between zinc and cadmium.

The closest resemblance exists between the properties of the transitional elements of the long periods, so that in Group 8 no subdivision is necessary.

37. The general formulas of the compounds of oxygen and hydrogen in Table VI are so written as to show the relative amounts of these two elements, in order to show the relationship existing between the different groups. This periodic reappearance of the properties of the elements applies also to their physical properties, such as, for instance, their electrical character, their ductility, malleability, melting point, etc., all of which appear to be in harmony with this law.

By means of the periodic table, Mendelejeff in 1871 was able to foretell the existence of an element which he called eka-aluminum, from the known properties of aluminum, indium, and zinc, the neighboring elements known to exist at that time. *Eka* signifies, next in order. He stated that it would have the following properties:

1. Atomic weight about 69.
2. A low melting point.

3. Specific gravity about 5.9.

4. Would not be acted on by air.

5. Would, when at a red heat, decompose water.

6. Would give an oxide, El_2O_3, a chloride, El_2Cl_6, and a sulphate, $El_2(SO_4)_3$.

7. Would form a potassium alum more soluble than aluminum alum.

8. The oxide should be more easily reducible than alumina, and the discovery of the metal by means of the spectroscope might be expected.

Now, the element gallium was discovered by Lecoq de Boisbaudran in 1875, and the properties it was found to possess were practically those of the eka-aluminum foretold by Mendelejeff. This is seen from the following:

1. Atomic weight 70.1.
2. Melting point 30.15°.
3. Specific gravity 5.95.
4. Only slightly oxidized at a red heat.
5. Decomposes water when at a high temperature.
6. Forms the compound, gallium oxide, Ga_2O_3; gallium chloride, Ga_2Cl_6; and gallium sulphate, $Ga_2(SO_4)_3$.
7. Forms a well-defined alum.
8. Was first detected by means of the spectroscope.

38. In the same manner, the properties of eka-boron and eka-silicon were foretold, corresponding to the elements scandium and germanium, which were discovered later, thus demonstrating the truth of the periodic law.

In the periodic table, the elements are arranged according to the increase in their atomic weights, but argon, tellurium, and thulium do not strictly conform to this condition. These may be true exceptions to the law, or, on the other hand, the apparent discrepancy may be due to the fact that they have not been obtained in a state of absolute purity, and this is exceedingly probable in the case of tellurium and thulium.

39. The position of hydrogen in the periodic table is a subject of considerable controversy. When one considers its electropositive nature, and the similarity of its salts (acids)

to those of the salts of the metals lithium, sodium, etc., it would seem that it should be placed in Group 1; at the same time it appears to fill a position also in Group 7 on account of its gaseous character, the absence of any metallic properties, and the diatomic nature of its molecules. It has therefore been placed, tentatively, in both positions in the table.

40. Classification Adopted.—As the elements are divided into natural groups, it would seem most logical to treat them in order, commencing with Group 1. There are several objections to this course, however, the chief one being the fact that in order to understand the chemistry of the first group, familarity with some of the later groups is essential.

But, in a general way, the periodic system will form the basis of the classification adopted for the study of this subject.

INORGANIC CHEMISTRY
(PART 4)

HYDROGEN AND OXYGEN AND THEIR COMPOUNDS

HYDROGEN

Symbol H. Atomic weight 1.008. Molecular weight 2.016. Valence I.

1. History.—Hydrogen was discovered by Paracelsus in the 16th century. In the year 1766, Cavendish, an English chemist, investigated this gas more thoroughly, and gave it the name of *inflammable air,* and by continued investigations in 1781 proved its elementary character. Lavoisier, finally, gave it the name of hydrogen.

2. Occurrence.—Hydrogen constitutes about one-ninth of the weight of water, the balance being oxygen; it is an essential constituent of all acids. It also occurs in organic matter, such as petroleum, animal, and vegetable materials, etc., combined with carbon, oxygen, nitrogen and sulphur in various proportions. Free hydrogen, while found in some volcanic gases, forms but a very small part of the hydrogen total. The air contains practically no free hydrogen.

3. Methods of Preparation of Materials.—Before describing the preparation of hydrogen, it may be well to state that there are two ways of preparing materials, so far as the chemist is concerned: The laboratory, or experimental, method and the technical, or commercial, method. The laboratory

method is confined to the preparation of small quantities for use in the laboratory, while the technical method is used to produce large amounts for industrial purposes. Experience has shown that laboratory methods are not always satisfactory when used as technical methods, on account of the cost, unsatisfactory condition of the products, mechanical difficulties, etc. On the other hand, many laboratory methods have been reproduced successfully on a large scale.

4. Laboratory Preparation of Hydrogen.—The most satisfactory laboratory method of obtaining hydrogen is by replacing the hydrogen in acids by a metal. Usually, hydro-

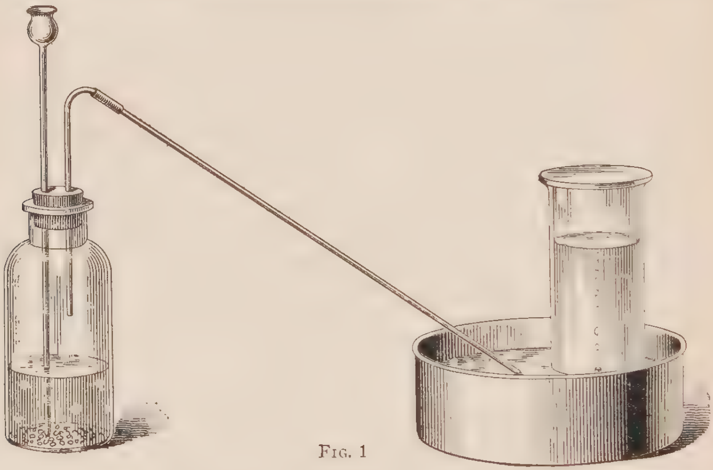


Fig. 1

chloric acid or sulphuric acid and iron or zinc are the materials used. Fig. 1 shows how the gas is generated and collected. A small quantity of a metal, zinc for instance, is placed in the bottle on the left and a two-holed rubber stopper is fixed into the neck of the bottle; a thistle tube is inserted through one hole and lowered until it is about $\frac{1}{4}$ inch from the bottom of the bottle. A bent tube is passed through the other hole and connected to a delivery tube by a piece of rubber tubing, which should fit tightly. The other end of this tube is arranged as shown in Fig. 2. The inverted bottle, shown in Figs. 1 and 2, is supported in the water on a beehive shelf, shown enlarged in

Fig. 3. The delivery tube passes through the opening in the side of the shelf. Either a basin or pan may be used to hold the water, as shown in Figs. 1 and 2, respectively. Water is

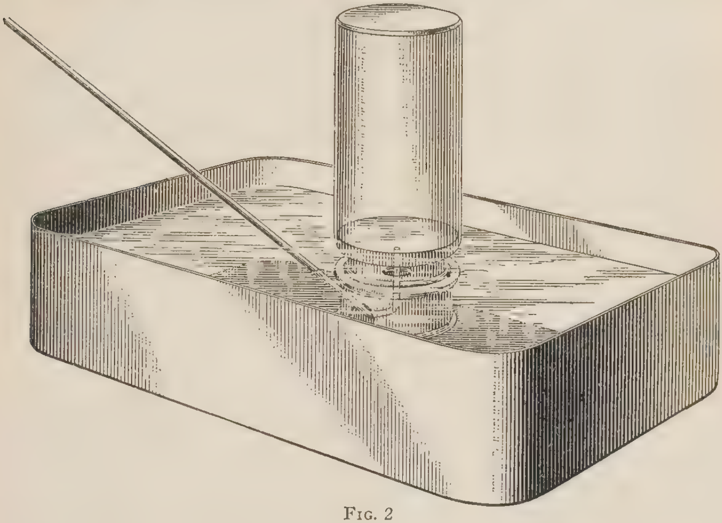


FIG. 2

used in the inverted bottle so that the gas, when collected above it, will be pure. As the gas passes through the water it displaces it, as shown in Fig. 1, and is obtained in a pure state. If water were not in the bottle, the gas would mix with the air in the bottle and would not be pure. The collecting bottle is filled to the top with water and the hand placed over the mouth of the bottle to prevent any loss of water. The bottle is then inverted into the basin filled with water, and the hand removed when the neck of the bottle is below the surface of the water. It is necessary that the apparatus should not leak, for the entrance of air into the apparatus may cause formation of an explosive hydrogen-air mixture. Whether all joints are air-tight or not may be determined by wetting them and blowing through the delivery tube with the palm of the hand pressed tightly over the top of the thistle tube. The appearance of bubbles at any connection indicates a leak at that point.

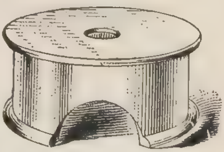


FIG. 3

5. After the apparatus is arranged as shown in Fig. 1, dilute sulphuric acid is gradually poured down the thistle tube until the surface of the acid in the generating flask is above the lower end of the thistle tube. Dilute sulphuric acid for this purpose may be made by slowly adding 1 part by volume of the concentrated acid to 6 parts of water. The solution should be stirred constantly during the addition of the acid. To avoid accidents, *water should never be added to concentrated sulphuric acid.*

Hydrogen is generated upon the addition of the acid to the metal and is carried over into the inverted bottle. Too much acid must not be added at one time, or else the chemical change will take place too rapidly and the mixture become too hot. If this does occur, a little water poured into the thistle tube and around the outside of the flask will cool it.

Care is taken to expel all the air from the apparatus before collecting the gas. The collecting bottle is not put into place until the hydrogen has driven out all of the air from the generating flask and connecting tube. Whether this is the case can be determined by holding an inverted test tube over the end of the delivery tube for about a minute or until all air has been driven from the tube. (All vessels containing hydrogen are held with the opening downwards to prevent the escape of the gas, for it is lighter than air.) The sample is then ignited by placing a flame at the mouth of the test tube and, if the gas burns quietly, it indicates that all air has been driven from the apparatus and the gas may be collected.*

6. Reactions.—The chemical change that takes place when sulphuric acid acts on zinc, can be represented by a chemical equation. Experiments have shown that zinc and sulphuric acid react chemically to form hydrogen and zinc sulphate. It has also been determined by analysis that 65.37 parts by weight of zinc react with 98.076 parts of sulphuric acid to form 2.016 parts by weight of hydrogen and 161.43 parts of zinc sulphate. In other words, 1 gram-molecule

*The student is not required to perform any of the experiments outlined in *Inorganic Chemistry*.

(the molecular weight in grams) of zinc and 1 gram-molecule of sulphuric acid react to form gram-molecular quantities of hydrogen and zinc sulphate. If an excess of sulphuric acid is added to 65.37 grams of zinc, only 98.076 grams of acid take part in the change, the excess being unaffected.

The valences of the elements taking part in this reaction afford excellent help in writing the equation representing it. For example, there are in 1 molecule of sulphuric acid 2 replaceable atoms of hydrogen, each of which has a valence of 1; these atoms can be replaced by either 2 atoms of a monovalent metal or 1 atom of a divalent metal. As zinc is a divalent metal, only 1 atom of this element is needed to free the 2 monovalent atoms of hydrogen from the acid. The left side of the equation will, therefore, be:

$$Zn+H_2SO_4$$

Experiments have shown that zinc sulphate and hydrogen are formed in this change. It, therefore, remains to determine how many molecules of each are produced. One zinc atom, Zn, can produce but 1 molecule of zinc sulphate, $ZnSO_4$, when it is acted on by sulphuric acid; likewise, 1 molecule of sulphuric acid can form but 1 molecule of hydrogen, H_2. The complete equation is, therefore,

$$Zn+H_2SO_4=ZnSO_4+H_2$$

7. Nascent and Molecular Hydrogen.—Hydrogen is assumed to exist in two forms, the one being described as nascent and the other as molecular. The nascent form, since it is supposed to be monatomic, is written H, while the molecular variety is written H_2. Nascent, or atomic, hydrogen is formed by the reaction between zinc and sulphuric acid, and the equation may therefore be written,

$$Zn+H_2SO_4=ZnSO_4+2H$$

Nascent hydrogen exists as such only momentarily and almost immediately changes to the molecular form. While in the active or nascent state, the element exhibits much greater chemical activity than when in the molecular form.

It should be realized, however, that nascent hydrogen has never been isolated and that the preceding explanation is purely theoretical. It is based upon the fact that hydrogen produced under certain conditions is more active than that produced under other conditions, and in order to distinguish the more active form, it is called nascent hydrogen.

8. Preparation of Hydrogen From Water.—Many metals can under proper conditions displace hydrogen in water. Only the active metals like sodium, potassium, and calcium can, however, displace it in cold water with any degree of rapidity. Sodium may conveniently be used to prepare hydrogen from water.

A piece of sodium about half the size of a pea, is placed in a basin of water. This operation is best accomplished by wrapping the sodium in a piece of filter paper. The metal should never touch the moist fingers. The sodium will appear to burn, will heat up the paper and cause it to ignite. This heat is produced when the chemical change between water and sodium takes place, and *in order to avoid violent explosions only very small quantities of sodium are used at a time.* After the action has ceased, no sodium remains, which fact can be explained by considering the chemical change that takes place.

Sodium has a greater attraction for oxygen than has hydrogen, that is, the chemical affinity between sodium and oxygen is greater than that between hydrogen and oxygen. The sodium can, therefore, take oxygen from the hydrogen in water. It has been found by experiment that sodium replaces but half the hydrogen in each molecule of water, forming hydrogen and a substance called sodium hydroxide, $NaOH$. The equation representing the formation of atomic hydrogen is in this case,

$$Na+H_2O=NaOH+H$$

and the molecular equation may be written,

$$2Na+2H_2O=2NaOH+H_2$$

This equation shows that 2 atoms, or molecules, of sodium (for each molecule contains but 1 atom) react with 2 molecules of water to form 2 molecules of sodium hydroxide and

1 molecule of hydrogen. The hydrogen gas, which passes off, can be collected, while the sodium hydroxide remains in solution.

9. Technical Production of Hydrogen.—The methods of preparing hydrogen so far described are for laboratory use. Within the last few years the commercial uses of hydrogen have been extended until its production has become an important industrial factor. There are now several successful technical methods of manufacturing hydrogen of which the following will be considered: (*a*) Iron-steam process, (*b*) Linde-Frank-Caro process, and (*c*) electrolytic process.

(*a*) *Iron-Steam Process.*—As previously stated, most metals can under proper conditions free hydrogen from oxygen in water. If iron, Fe, for example, is heated to 800° C. and steam is passed over it, hydrogen and ferrous oxide, FeO, are formed, as shown by the equation:

$$Fe+H_2O=FeO+H_2$$

The hydrogen is collected and the ferrous oxide is changed back into iron so that it can be used over again, by subjecting it to the action of water gas, which consists of about 50 per cent. of hydrogen, 40 per cent. of carbon monoxide, CO, and 10 per cent. of impurities. The change that takes place when ferrous oxide is acted on by water gas, is shown by the equation:

$$2FeO+CO+H_2=2Fe+CO_2+H_2O \text{ (steam)}$$

In this equation it is shown that for every 2 molecules of ferrous oxide used, 1 of hydrogen and 1 of carbon monoxide are needed, and that 2 molecules of iron (each molecule of iron contains 1 atom), 1 of carbon dioxide, and 1 of water are formed.

(*b*) *Linde-Frank-Caro Process.*—This process depends upon the fact that carbon monoxide and hydrogen liquefy at different temperatures. Water gas, which consists mainly of carbon monoxide and hydrogen, is cooled and compressed until the carbon monoxide changes to a liquid, leaving the hydrogen in a gaseous form. Carbon monoxide becomes a liquid at a temperature of −192° C., while hydrogen remains a gas until

a temperature of $-253°$ C. is reached. The water gas is made by passing steam over red-hot coke. The reaction is as follows:

$$C + H_2O \text{ (steam)} = CO + H_2$$

Each molecule of water or steam is converted by one of carbon into one molecule of carbon monoxide and one of hydrogen.

10. The Electrolytic Production of Hydrogen. When pure, distilled water is decomposed into its two elements by electricity, it is evident that only pure oxygen and hydrogen will be obtained and of recent years the apparatus or generators which have been developed for the purpose of producing these two gases on a commercial scale have reached a high state of efficiency. Fig. 4 shows one of the latest types of oxygen-hydrogen generator as it looks from the outside and set up for operation, while Fig. 5 gives an idea of the internal construction of the generator, and shows how the water is actually electrolyzed and the gases produced. The letters used on each illustration are the same for similar parts.

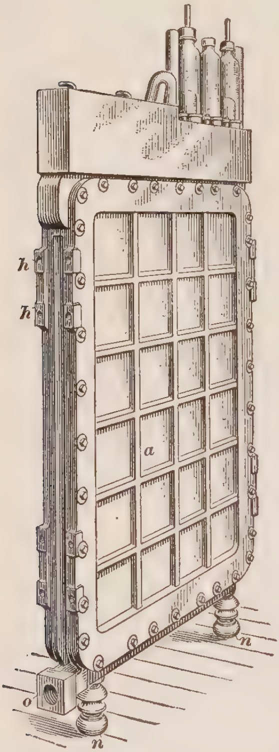


FIG. 4

Mechanically, the generator consists of a cast-iron body or shell *a*, which rests on the adjustable insulating bases *n*, and which is provided with a drain *o*, at the bottom so that the electrolyte may be drained when desired. The electrical connections are made by means of the bus-bars shown at *h*. The interior of the generator shell is divided into two vertical compartments by a partition or diaphragm *b* of pure, woven asbestos. On one side of the generator and insulated from the shell is a nickel-plated, cast-iron electrode shown at *c*. This constitutes the anode on which the oxygen is

generated. Likewise, on the other side of the shell is another electrode *d*, made of plain cast iron. This is the cathode on

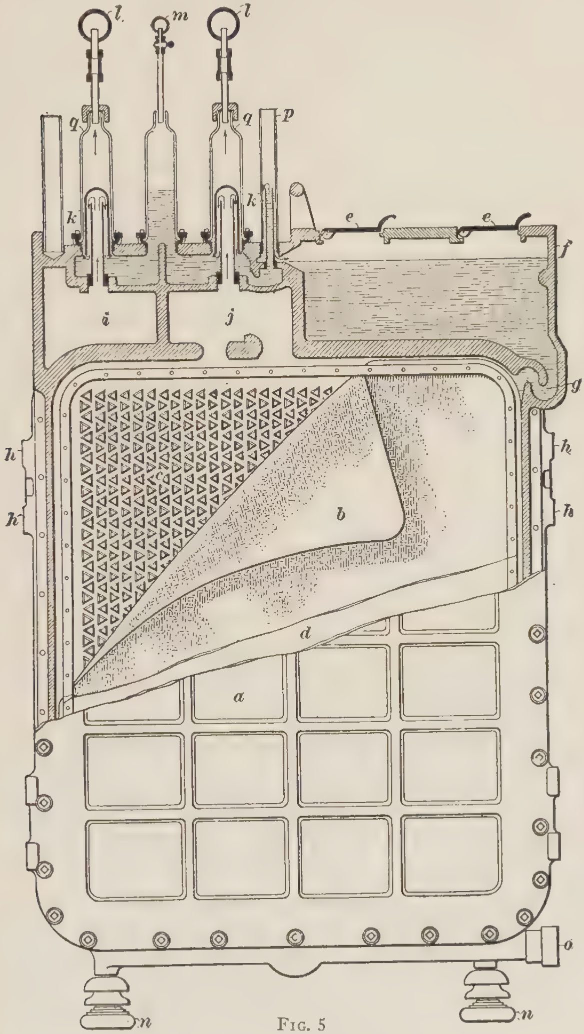


Fig. 5

which the hydrogen is generated and it is also insulated from the generator shell. The two electrodes are therefore insulated not only from each other but also from the body casting.

11. Operation of the Generator.—The interior of the generator is first filled with a solution of caustic soda, $NaOH$, or caustic potash, KOH, in distilled water, through doors *e*, which are also used for inspection purposes. This solution constitutes the electrolyte. When the current is caused to flow through the electrolyte, the production of hydrogen and oxygen begins immediately, each gas being liberated on opposite sides of the asbestos diaphragm. It should be remembered at this point that during the operation of the generator, the distilled water only is decomposed into its constituent gases, the dissolved caustic potash or caustic soda merely serving to increase the conductivity of the solution, since pure water is not a good conductor of electricity. During the operation, the level of the electrolyte is kept at *f*, as shown in Fig. 5, by adding from time to time distilled water through the water feed at *m*. The gases are prevented from escaping through the doors *e*, because of the liquid seal at *g*.

12. The gases evolved at the electrodes rise through the electrolyte, the oxygen on one side of the diaphragm and hydrogen on the other. The former then passes into chamber *i*, and the latter into the chamber *j*. Both gases then pass through their respective water-sealed gas traps *k*, as indicated by the arrows, which are surrounded by glass bell-jars *q*, which allow the operator to observe the flow of gas as it bubbles from each trap. From the traps the gases leave the generator at the offtakes *l*, and then pass through a manifold, which is merely a collecting device for two or more generators, and then into the gas main leading to the gas holder. The pipes *p* are overflow pipes.

In practice, single generators are not used but are connected together in banks consisting of from 10 to 500 generators or units. In a general way Table I shows the output which has been obtained from several batteries of generators. Economy of output, however, depends upon the manner in which the different units are connected electrically, and this phase of the subject is too technical to be gone into in this description.

TABLE I

CAPACITY OF GENERATORS

Number of Generators	Operating at 600 Amperes			Operating at 800 Amperes			Operating at 1,000 Amperes		
	Cubic Feet Per 24 Hours		Voltage Required	Cubic Feet Per 24 Hours		Voltage Required	Cubic Feet Per 24 Hours		Voltage Required
	Oxygen	Hydrogen		Oxygen	Hydrogen		Oxygen	Hydrogen	
10	1,152	2,304	25	1,536	3,072	30	1,920	3,840	30
25	2,880	5,760	60	3,840	7,680	60	4,800	9,600	60
50	5,760	11,520	110	7,680	15,360	115	9,600	19,200	120
100	11,520	23,040	110 or 220	15,360	30,720	115 or 230	19,200	38,400	120 or 240
200	23,040	46,080	110 or 220	30,720	61,440	115 or 230	38,400	76,800	120 or 240
300	34,560	69,120	110 or 220	46,080	92,160	115 or 230	57,600	115,200	120 or 240
500	57,600	115,200	110 or 220	76,800	153,600	115 or 230	96,000	192,000	120 or 240

13. Chemical Properties of Hydrogen.—Hydrogen is not an extremely active element, its degree of activity depending upon physical conditions such as temperature, pressure, the presence of catalytic agents, etc. It combines with oxygen to form water, but the combination takes place very slowly at temperatures below 500° C.; while at 750° C., or at about red heat, combination takes place with explosive violence.

Water is the sole product of the combustion of hydrogen in atmospheric air or oxygen, hence its name hydrogen, which is derived from the Greek words meaning water producer.

$$2H_2+O_2=2H_2O$$

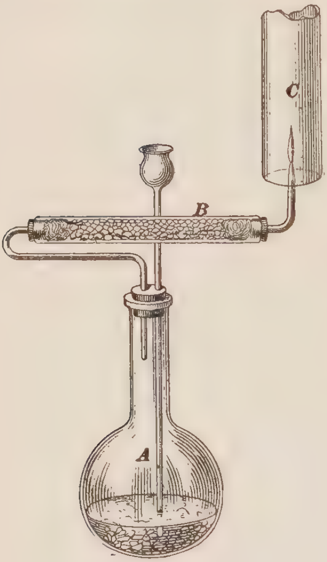


FIG. 6

As all gases obtained from mixtures in which vapor is present contain a certain quantity of aqueous vapors, it is necessary to dry the hydrogen before attempting to prove the presence of water as a result of its combustion. This is accomplished by passing the gas that is to be dried, over some substance that possesses a strong affinity for water. The most important desiccating, or drying, agents used in the laboratory for drying gases, liquids, and solids are anhydrous calcium chloride and concentrated sulphuric acid. Which of these is the more suitable depends, of course, on the nature and properties of the gas to be dried; hydrogen, for instance, may be dried by being passed through either calcium chloride or sulphuric acid.

14. In order to show that water is the sole product of the combustion of hydrogen in oxygen, the apparatus illustrated by Fig. 6 may be used. This apparatus consists of a flask A fitted with a two-hole rubber stopper through which is passed a thistle tube and the delivery tube. The delivery tube is con-

nected to the tube *B*, which contains dry or anhydrous calcium chloride. The hydrogen is generated in the flask *A* by the action of hydrochloric or sulphuric acids on zinc, and dried by passing through the tube *B*. It is then burned at the jet within the large glass tube *C*, which should be about 18 inches in length. The water vapor produced by the combustion of the hydrogen is condensed on the inside walls of this tube.

Too much stress cannot be laid on the injunction to first see before lighting the jet, that a collected test tube of the gas burns quietly. Neglect of this test may lead to an explosion.

This experiment is often accompanied by a peculiar musical note produced by a rapid series of small explosions within the long tube.

15. Finely divided platinum causes a reaction to take place between hydrogen and oxygen, by its mere presence; it acts by contact, is unaffected when the chemical change is completed, and may therefore be called a catalytic agent. It causes the reaction between hydrogen and oxygen, slow at ordinary temperatures, to proceed with such rapidity that the platinum becomes white hot, thus causing the mixture to ignite or explode. Gas lighters such as are used in some laboratories, and automatically lighting gas jets are constructed on this principle. If the hydrogen flame is allowed to play on a piece of calcium oxide, commonly called quicklime, it yields a dazzling white light, generally known as calcium light, or limelight.

Small quantities of hydrogen usually ignite with a small explosion which sounds not unlike that heard when a bottle is uncorked. This fact serves as one means of identifying the gas when it is mixed with air or oxygen.

16. Relative Activity of Metals and Hydrogen. Hydrogen, which acts chemically like metals (these will be considered in another Section), possesses greater chemical activity than some metals and less than others. Table II shows the relative activity of the common metals and hydrogen. All the metals more active than hydrogen, that is, all the metals from

potassium to lead can replace hydrogen in dilute acids, and, in some cases, in water; the metals from antimony to gold, however, cannot replace hydrogen in dilute acids or water. For example, potassium replaces hydrogen in water with great activity, as shown in the equation:

$$2K+2H_2O=2KOH+H_2$$

Sodium replaces hydrogen in water in a similar way, but the action is not as vigorous as in the case of potassium. Magnesium reacts with superheated steam as does iron, but neither decompose boiling water to any extent. Zinc replaces the hydrogen of acids, as has already been shown, but the metals from antimony to gold do not replace hydrogen from either dilute acids or water.

TABLE II

RELATIVE CHEMICAL ACTIVITY OF METALS

Most Active Metals	Least Active Metals
Potassium	Antimony
Sodium	Bismuth
Calcium	Copper
Magnesium	Mercury
Aluminum	Silver
Chromium	Platinum
Manganese	Gold
Zinc	
Iron	
Nickel	
Tin	
Lead	
Hydrogen	

This table of relative activity of metals is well worth remembering, for the relation holds good, as will be shown later, for many other chemical reactions.

17. Physical Properties of Hydrogen.—Pure hydrogen is a colorless, odorless, and tasteless gas, and is the lighest substance known, its specific gravity being .06949 (air=1). It is only slightly soluble in water, 100 volumes of the latter dissolving 2.1 volumes of the gas at 0.5° C. This means that 100 cubic centimeters of water dissolves 2.1 cubic centimeters of hydrogen at 0.5° C.

Hydrogen may be liquefied by reducing its temperature to −240.8° C., and at the same time subjecting it to a pressure of about 14 atmospheres. In other words, its critical temperature

is $-240.8°$ C., and the critical pressure is approximately 14 atmospheres. By subjecting hydrogen to pressure at very low temperatures it may even be solidified.

In 1898, Dewar succeeded in liquefying hydrogen in sufficient quantities to learn the properties of the liquid. It is colorless and boils at $-252.8°$ C. Its specific gravity as compared with water is .07, this being much less than the specific gravity of any other liquid.

By its own rapid evaporation liquid hydrogen is frozen to a white solid mass, melting at $-259°$ C. By the rapid evaporation of this solid a temperature of $-260°$ C. has been obtained. Without exception all the known gases have been liquefied by cooling with liquid hydrogen.

18. Among other physical properties that hydrogen possesses must be mentioned its remarkable faculty of passing through plates of iron and platinum at high temperatures. According to Graham, who thoroughly investigated this phenomenon, and named it diffusion, which property is closely related to that of absorbing hydrogen, and which is possessed by a number of solid bodies, and particularly metals, such as platinum, iron, and palladium. Palladium, especially, is distinguished by its energy to absorb, or occlude, hydrogen. Graham has shown that there is no necessity of assuming that porosity in the structure of the metals accounts for this phenomenon, but that it is due to the fact that such metals absorb the hydrogen and yield substances that still retain characteristic metallic properties, but readily evolve part of the absorbed gas when heated. The last traces, however, can be driven off only at a red heat in vacuo. After the absorption of hydrogen, the metal presents the same appearance as before, but some of its physical properties are slightly changed. Thus, in the case of palladium, the metal becomes more magnetic and its electric conductivity is reduced. At a red heat palladium will absorb or occlude, 900 times its own volume of hydrogen, with an increase of 1.6 per cent. in the volume of this metal. To this absorbed form of hydrogen Graham gave the name *hydrogenium,* concluding that although

the hydrogen did not combine chemically with the metal, it did assume the solid form, acting as a semimetal and giving rise to an alloy such as is obtained when sodium and mercury are brought together.

19. Pure hydrogen burns with a non-luminous and colorless flame at ordinary pressure, but its luminant power is increased as the atmospheric pressure is increased. Though non-luminous at ordinary temperatures, its flame evolves a great amount of heat. It is combustible, but not a supporter of combustion; a lighted candle plunged into a jar filled with hydrogen is at once extinguished. It does not support respiration—animals die when confined in it; it should, however, not be assumed from this fact that the gas is poisonous, for the cause of death is simply a lack of oxygen which is necessary to animal life.

Hydrogen cannot be stored in any vessel having the slightest crack or flaw, or it will pass through it with a much greater readiness than air. This property is described by saying that hydrogen is very diffusible.

20. One of the difficulties met with in handling hydrogen in commercial work has been the tendency of the gas to leak out of apparatus and through walls of containers and tanks which, however, were tight to air and steam under pressure. A large steel tank tested to 150 pounds air pressure, leaked badly when hydrogen was introduced at 60 pounds pressure. A cylinder fitted with a stuffingbox tested to 120 pounds steam pressure, made a very efficient whistle when hydrogen was introduced at 60 pounds pressure.

The ability of nascent hydrogen to penetrate may be illustrated by the following: If it is generated by immersing an iron tube which is sealed at both ends, in a dilute acid solution such as sulphuric acid, some of the gas will pass from the outside wall of the tube through the iron and may be collected by suitable means from the inside of the tube. The rate of penetration of iron by hydrogen increases with the temperature. Copper is not penetrated, but it has been demonstrated that a coating of tin on the iron increases the rate of penetration.

21. Uses of Hydrogen.—Because of its great buoyancy, hydrogen has long been used for the filling of balloons and, more recently, for dirigibles. For this purpose, however, hydrogen possesses the serious disadvantage of being extremely inflammable and numerous explosions of balloons have been caused either by atmospheric electricity or by sparks from the power plant of the dirigible, and during the recent World War, due to the development of incendiary projectiles, the operation of hydrogen-filled balloons was a hazardous undertaking. The manner in which the dangers attending the use of hydrogen in balloons were finally overcome, will be discussed under the properties of the element helium.

Another important use to which hydrogen has been put is the cutting and welding of metals, particularly iron and steel, by means of the oxyhydrogen cutting and welding torch. Hydrogen is also used extensively for the hydrogenation of oils. This process consists of passing hydrogen through an oil like cottonseed oil, to which has been added finely divided nickel, which acts as a catalytic agent. The resultant product of the reaction between hydrogen and the oil has the consistency of lard or butter and for certain purposes it may be used as a very satisfactory substitute for these substances.

Oils having a disagreeable odor or taste, such as fish oils and castor oil, may be made odorless and practically tasteless by passing hydrogen through them, and for this purpose it is not necessary to use a catalytic agent.

OXYGEN

PROPERTIES, PREPARATION, AND COMBINATIONS

Symbol O. Atomic weight 16. Molecular weight 32. Valence II.

22. History.—Doctor Priestley, of Birmingham, England, discovered in 1774 that by heating mercury in contact with air in a closed vessel, the amount of air present was lessened, and that red scales were formed on the surface of the mer-

cury. He found that the red scales thus produced consisted of mercury and a gas which he named dephlogisticated air. The following year, 1775, Scheele, a Swedish chemist, discovered independently the same gas, which he named empyreal air. Condorcet called it vital air, and in 1781 Lavoisier named it oxygen from the Greek words for *acid former*. Up to Lavoisier's time, the phlogiston theory, proposed by Stahl, was generally accepted. According to this theory, every combustible substance contained something called phlogiston, which in

FIG. 7

escaping caused the phenomenon known as combustion, or burning. It was from this theory that Priestley derived his name for oxygen, and though he proved its elementary character, the name indicates that he did not well understand its real nature. Lavoisier disproved the phlogiston theory and showed that combustion is a union with oxygen.

23. Occurrence.—Oxygen is the most abundant of all elements. In the free state it forms about one-fifth, by volume, of the air. Chemically combined with hydrogen it

forms eight-ninths, by weight of water; united with other elements it constitutes about one-half the rocks in the earth's crust and over one-half of animal and vegetable matter.

24. Laboratory Preparation.—If mercuric oxide, *HgO*, is gently heated, it decomposes into the elements mercury and oxygen. The mercury remains behind as a liquid and the oxygen passes off as a gas. This change or reaction may be produced in a simple way. If a small amount of mercuric oxide, which is a red powder, is heated in a test tube, Fig. 7, the sides of the tube become lined with a mirror of mercury which after a short time separates into little drops. If a match previously lighted and extinguished but still bearing a tiny spark at the end, is thrust into the mouth of the tube, it at once reignites and burns brightly. This is known as the spark test for oxygen and is well worth remembering, for it serves as a simple means of detecting oxygen.

This method of making oxygen, though of historical interest, is too expensive to be used as a regular means of preparation. The reaction is $2HgO = 2Hg + O_2$.

The most convenient method of preparing oxygen is to heat gently potassium chlorate, $KClO_3$, which readily breaks up into potassium chloride, KCl, and oxygen. The course of the reaction may be represented by the equation,

$$KClO_3 = KCl + 3O$$

But, according to the table of atomicities, oxygen is diatomic and the molecule must be written O_2; therefore, the correct equation would be

$$2KClO_3 = 2KCl + 3O_2$$

By inspection, it may readily be ascertained that there are the same number of atoms of each element on each side of the equality sign.

25. The preparation of oxygen can also be effected by using an arrangement such as is shown in Fig. 8. Sufficient potassium chlorate, a white solid, is placed in the test tube *A* to fill the bottom of the tube to the height of ½ inch and heat is then gently applied. The substance crackles and the crystals split up. This explosive splitting up of crystals when heated

is called decrepitation. The potassium chlorate gradually melts and appears to boil, at which point it breaks up easily with the liberation of oxygen. The spark test already described may be used to prove the presence of oxygen.

It has been found that the presence of manganese dioxide, MnO_2, causes potassium chlorate to decompose and liberate oxygen more readily and at a lower temperature than when it is absent. While potassium chlorate alone does not give off oxygen below 351° C., the mixture of potassium chlorate and manganese dioxide gives it off readily at 200° C.

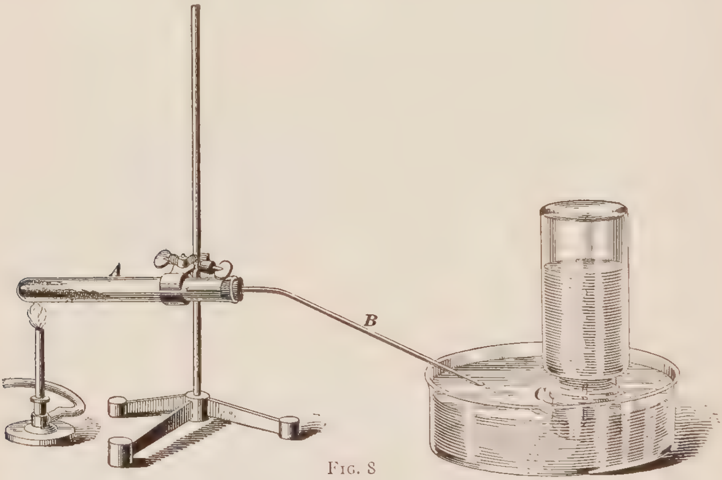


FIG. 8

26. The manganese dioxide acts merely by its presence in some undetermined manner and is not itself affected; it may, therefore, be called a catalytic agent. It has been determined experimentally that the highest yields of oxygen are obtained by using 1 part by weight of manganese dioxide with 3 parts by weight of potassium chlorate. Heating a mixture of potassium chlorate and manganese dioxide is usually resorted to when a small quantity of oxygen is needed in the laboratory and there is no other supply available.

27. Preparing and Collecting Oxygen.—The 6-inch tube *A*, Fig. 8, is filled about one-third full of the potassium chlorate-manganese dioxide mixture, and a wire is pushed

through the mixture to the bottom of the tube to make a passage for the oxygen evolved. The tube is then connected to a delivery tube *B* by means of a tightly fitting stopper, and is adjusted so that the delivery tube extends into the trough to the side opening of the beehive shelf.

The collecting bottle filled to the brim with water is then put in position by placing the palm of the hand over the mouth of the bottle, inverting the bottle, placing the neck of it under the surface of the water in the trough, without losing any of the water in the bottle, and then removing the hand. Care

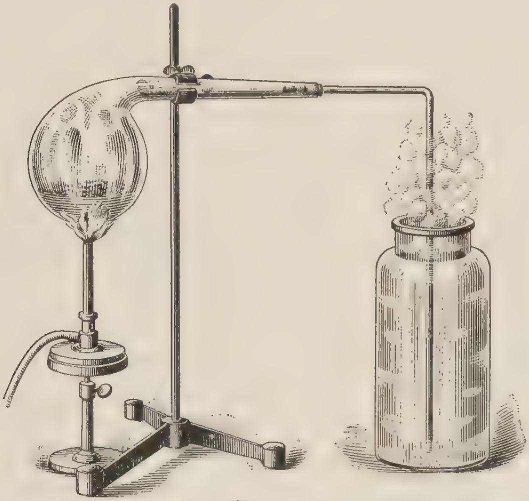


Fig. 9

must be taken to keep the neck of the water-filled bottle under the surface of the water in the trough lest some of the water should escape from the bottle and be replaced by air.

The mixture in the test tube is gently warmed at the end near the stopper and the flame is brought slowly toward the other end of the tube as oxygen is evolved. This procedure prevents clogging of the delivery tube with loose dust carried over by the current of oxygen. The burner is withdrawn from the test tube when the bottle is two-thirds full of oxygen, and the end of the delivery tube is withdrawn from the water as soon as the bottle is full of oxygen; otherwise, the contraction

of the gas as it cools in the apparatus, would draw water into the test tube and cause it to crack. The bottle containing oxygen is placed with its mouth upwards, for oxygen is heavier than air, and the bottle is covered with a piece of glass to insure the retention of the gas.

28. Collection of Gases.—In the foregoing article, the method of collecting oxygen by displacing water in a bottle, was described. This method is suitable for all gases that are insoluble or slightly soluble in water; it cannot, however, be used for soluble gases, for the water would absorb the gases and in this way retard their collection. Inasmuch as the collection of gases is an operation constantly applied by chemists in some lines of work, a description of some of the methods used will not be out of place.

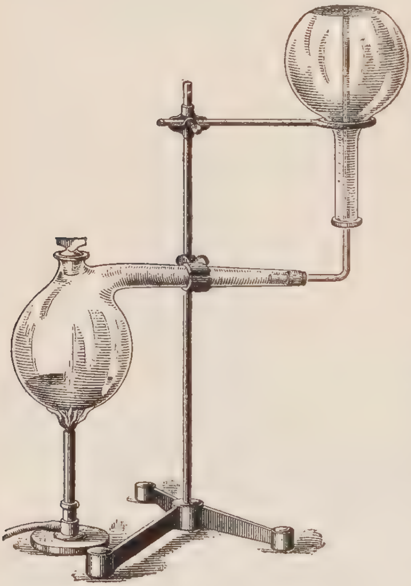


Fig. 10

Gases, insoluble or slightly soluble in water, are collected by the displacement of water as described in the preceding article. Gases soluble in water may be collected by the displacement of mercury, an operation that is exactly the same as by the displacement of water, excepting that mercury is used instead of water. In many cases, the use of mercury is neither convenient nor desirable, whereupon gases are collected by the displacement of air. If a gas is heavier than air, it is collected by the upward displacement of air, as is shown in Fig. 9.

If it is lighter than air, it is collected by the downward displacement of air as is shown in Fig. 10. In the upward

displacement of air, the gas to be collected is delivered to the bottom of a bottle standing upright and the air in the bottle is forced up and out. In the downward displacement of air, the gas to be collected is passed into an inverted bottle and the air in the bottle is forced down and out. Other methods of collecting gases may sometimes be used but the methods described are those in common use.

29. Commercial Preparation of Oxygen.—Oxygen is obtained commercially from water and air, for these are the most abundant of all sources, and oxygen can be extracted from them in a practical and economical way.

The electrolytic process for the manufacture of oxygen has already been described. In another method, porous barium oxide, BaO, is used in one process to take oxygen from the air under one set of conditions and give it up under another. Originally, barium oxide was heated to a dull redness in a current of air free from carbon dioxide, CO_2, to form barium dioxide, BaO_2, as follows:

$$2BaO+O_2=2BaO_2$$

The heat was then raised to a bright redness to decompose the barium dioxide into oxygen, which was collected, and barium oxide, which was used again. The reaction is as follows:

$$2BaO_2=O_2+2BaO$$

Owing to the fact that the barium oxide became non-porous and glassy after it had been used several times, and so was no longer able to take up oxygen, the process was too expensive to be worked on a commercial scale.

30. Brin Process.—In this process the objectionable feature of the preceding process has been overcome. This method consists in heating barium oxide to a dull redness in retorts while forcing pure air in under a pressure of about 15 pounds per square inch. As soon as the barium oxide has been changed to barium dioxide, the pressure pump is reversed and the air is exhausted from the retort to produce a vacuum. The temperature is not changed. Under these conditions the

barium dioxide breaks up into oxygen, which is collected, and porous barium oxide, which can be used continually for six months before it needs to be renewed. This process is a commercial success.

The formation of barium dioxide from oxygen and barium oxide, and the decomposition of barium dioxide to form barium oxide and oxygen, is an excellent illustration of a reversible reaction.

31. Linde Process.—Oxygen can also be obtained from liquid air. Machines of special design have been perfected so that air can be liquefied economically. In these various types of apparatus air is compressed by means of powerful pumps and the temperature of the compressed gas is lowered enough by allowing a small portion of the gas to expand in such a way that the heat necessary to produce the expansion is largely withdrawn from the rest of the gas, thereby cooling the latter.

Liquid air is essentially a mixture of nitrogen, which boils at −195.5° C., and liquid oxygen, which boils at −182.7° C. The temperature of the liquid air is so adjusted that it is kept above −195.5° C. and below −182.7° C., under which condition the nitrogen evaporates and the oxygen remains. In this process an oxygen product containing less than 10 per cent. of nitrogen can be produced.

32. Tessie du Motay-Maréchal Process.—The Tessie du Motay-Maréchal process is also used to produce oxygen. If a mixture of manganese dioxide, MnO_2, and sodium hydroxide, $NaOH$, is heated to dull redness in a current of dry air, sodium manganate, Na_2MnO_4, is formed, thus:

$$2MnO_2+4NaOH+O_2=2Na_2MnO_4+2H_2O$$

This material in turn liberates oxygen when it is heated to 450° C. in a current of steam, H_2O, as shown in this reaction:

$$2Na_2MnO_4+2H_2O=2MnO_2+4NaOH+O_2$$

The oxygen is collected and the manganese dioxide and sodium hydroxide are used to absorb more oxygen.

The equations in this case are interesting, for they bring out a few important points. The change is a reversible one and can, therefore, be written as:

$$2Na_2MnO_4+2H_2O \rightleftharpoons 2MnO_2+4NaOH+O_2$$

These equations also show that, in some cases, the change that takes place when certain chemicals unite, will vary with conditions. In dry air and at dull red heat, one change takes place; in a current of steam and at 450° C., the exactly opposite change occurs. It is apparent, therefore, that there are chemical changes that cannot be predicted with any degree of accuracy unless the exact conditions under which the substances react are known.

33. Chemical Properties of Oxygen.—Chemically, oxygen is one of the most active of the elements. It enters into combination with all elements with the exceptions of fluorine and members of the helium group, but it does not unite directly with chlorine, bromine, or iodine. All substances that burn in air burn with greatly increased vigor and brilliancy in pure oxygen. Thus, if either carbon, sulphur, or phosphorus is heated to the burning point and then placed in an atmosphere of pure oxygen, each burns very vigorously, the oxides of the elements being produced in each case.

C	+	O_2	=	CO_2
carbon (charcoal)		oxygen		carbon dioxide
S	+	O_2	=	SO_2
sulphur		oxygen		sulphur dioxide
P_4	+	$5O_2$	=	$2P_2O_5$
phosphorus		oxygen		phosphorus pentoxide

Ordinary iron rusts when exposed to moist air, ferric oxide, Fe_2O_3, being formed, but if a piece of thin iron wire is heated in a flame until it is white hot, and is then plunged into a jar of oxygen, the iron will burn with a dazzling light, magnetic oxide of iron, Fe_3O_4, being formed.

$$3Fe+2O_2=Fe_3O_4$$

An idea of the great chemical activity of oxygen can best be obtained, however, by a study of the different compounds in which it is contained.

34. Physical Properties of Oxygen.—Oxygen is a colorless, tasteless, and odorless gas, with a specific gravity of 1.10535, which is a little heavier than air. It is slightly soluble in water, 4.9 volumes of oxygen dissolving in 100 volumes of water at 0° C.; and 2.6 volumes of oxygen in 100 volumes of water at 30° C. The critical temperature and pressure of oxygen are respectively −118.0° C., and 49.3 atmospheres. Liquid oxygen is pale-blue in color, is strongly attracted by a magnet, and boils at −182.7° C.; the liquid may be frozen to a solid which melts at −227° C.

The foaming and spitting of molten silver upon solidification and blistering upon rolling, are due to dissolved oxygen. Investigations have shown that the volume of oxygen which 10 grams of melted silver at 1,020° C., and 751 millimeters pressure will dissolve, is 20.5 cubic centimeters. Brass ingots which have been poured at too low a temperature, and metal which has been rolled and annealed, are sometimes brittle and unsatisfactory owing to the presence of oxygen.

35. Oxygen does not burn, but it acts as a supporter of combustion. It is necessary for the breathing of man and animals, for without it suffocation would result. Atmospheres that are deficient in oxygen begin to affect men when the per cent. of oxygen is about as low as that affecting canaries and mice. Canaries are slightly more susceptible than mice to a deficient supply of oxygen. In mixtures of nitrogen and oxygen, containing about 7.6 per cent. to 7.8 per cent. of the latter, canaries begin to exhibit pronounced distress, and only when the oxygen content falls as low a 7.0 per cent. do mice show considerable distress and with this oxygen content a man is in great danger of dying. Therefore, canaries and mice should not be used by exploring parties in mines or long tunnels to indicate the point at which men not equipped with breathing apparatus should retreat. Pure oxygen may be inhaled for a short time without injurious effects being

observed, and it is frequently administered in cases of partial suffocation with good results. The prolonged breathing of pure oxygen, however, is dangerous, since the normal temperature of the body is soon exceeded.

36. Uses of Oxygen.—The oxygen of the air is an indispensable agent in the generation of light and power from fuels. Without it, combustion of coal, wood, oils, and other fuels would be impossible. Atmospheric oxygen also combines with other elements in a wide variety of ways to help sustain life, for it serves as a means whereby the energy of living beings is stored up and then used. It is an indispensable adjunct to the world, for without it living things could not exist.

37. Oxygen is used to a great extent in the oxy-hydrogen and oxy-acetylene cutting and welding torch. In the operation of lead burning whereby joints are made in lead sheets and other objects of lead by merely melting and joining the edges of the material without the use of a solder, the oxygen-gasoline system has been successfully used. By the use of this system, more perfect combustion and higher temperatures can be obtained, and it is claimed that a much better quality of work can be turned out at less cost than by the older hydrogen-air system.

An interesting use to which liquid oxygen has recently been put is as an explosive. In the process, a cartridge made of paper is charged with carbon, petroleum, and liquid oxygen, the finished cartridge, which, of course, can only be charged shortly before use, due to the high volatility of liquid oxygen, is fired electrically. Oxygen is also used in first-aid work around mines, in the manufacture of oils, in the aging of liquors, in the refinement of glass, and for medicinal purposes.

OXIDATION AND REDUCTION

38. Oxidation and Oxidizing Agents.—The process in which oxygen unites with other substances is called *oxidation*. This action may be slow, as in the rusting of iron, or rapid, as in the burning of carbon. The product formed by

the chemical combination of oxygen and any other element is called an *oxide*. For example, PbO is lead oxide, SnO is stannous oxide, K_2O is potassium oxide, and H_2O, commonly called water, is hydrogen oxide.

An **oxidizing agent** may be defined as a substance that causes an element or compound to combine with oxygen or which causes an increase in the valence of an element. The following are common examples of oxidizing agents and their reactions:

(1) $$4Fe+3O_2=2Fe_2O_3$$

(2) $$2FeCl_2+Cl_2=2FeCl_3$$

In the first equation, metallic iron is oxidized to ferric oxide and in the second equation, ferrous chloride is oxidized to ferric chloride, the valence of iron being increased in each case. Oxygen and chlorine in these reactions are then properly called oxidizing agents.

39. Combustion.—The term combustion, in its broad meaning, is applied to processes in which substances combine vigorously with an evolution of light and heat, though most commonly it is considered as an oxidizing process, because it is a vigorous combination of a substance with oxygen with the evolution of light and heat. This action is also called *burning*. The lowest temperature at which a substance ignites is called the kindling point of that substance. Each substance has its own kindling point. For example, wood may be exposed to the action of oxygen for years without burning. If, however, the temperature is raised to the kindling point, the wood at once ignites and burns vigorously with the evolution of light and heat.

40. Reduction and Reducing Agents.—The action opposite in its effects to that of oxidation is termed a reduction, and is defined as the process in which oxygen is taken from substances. For example, when hydrogen and cupric oxide react chemically, the hydrogen takes oxygen from the cupric oxide to form copper and hydrogen oxide (water); thus,

$$CuO+H_2=H_2O+Cu$$

Hydrogen acts as a reducing agent in this change, because it takes oxygen from cupric oxide; that is, it reduces cupric oxide to copper. Cupric oxide can, in this case, be considered an oxidizing agent, for it oxidizes hydrogen to hydrogen oxide, or water.

41. Reducing Agents.—The native compounds or ores, from which metals are derived, are in many cases oxides or sulphides of such metals. The process used to obtain these metals in a free or uncombined state is known as the reduction of the ore to its metallic state. From this a **reducing agent** may be defined as a substance that removes oxygen or elements similar to it, from compounds, or that decreases the valence of an element, changing it from a higher to a lower state of oxidation.

Owing to the readiness with which hydrogen combines with oxygen, it is one of the most prominent and powerful reducing agents. Thus, if hydrogen is passed over red-hot iron oxide, the metal is obtained in the free state, according to the following equation:

$$Fe_2O_3+3H_2=2Fe+3H_2O$$

The following equation illustrates what is meant by a decrease in valence:

$$2FeCl_3+SnCl_2=2FeCl_2+SnCl_4$$

In this reaction ferric chloride is reduced to ferrous chloride by means of stannous chloride, which in turn is oxidized to stannic chloride.

OZONE

Allotropic oxygen. Formula O_3. Molecular weight 48.

42. History.—Van Marum in 1785 first noticed that a peculiar, fresh, penetrating odor was given off around electrical machines in operation, but it was not until 1840 that the source of this odor was determined. In that year Schönbein proved that it was due to the formation of a gas containing three atoms of oxygen to the molecule. The formula of ozone

is written O_3, but the exact structure of the molecule and the valence of the oxygen atoms have not yet been determined.

43. Occurrence.—Ozone probably occurs free in the atmosphere after electrical disturbances, and its odor is noticeable after thunderstorms accompanied by violent electric discharges. Its presence has also been noted around electrical generators.

44. Preparation of Ozone.—Ozone is difficult to make. It is *endothermic* which means that it absorbs heat during the process of its formation. The temperatures of formation and decomposition are very much the same, so that although heat is necessary for the formation of ozone, it must also be kept away from the gas after it has been formed. In other words, when the ozone has been formed, it must be removed from the reaction zone immediately or it will decompose into oxygen.

Ozone may be made chemically, mechanically, or electrically, but the first two methods are of no practical importance. The electrical method, however, has been developed to the extent that it is no longer in the experimental stage but may be termed a commercial proposition, as will be evident by observing the uses to which ozone generated by this method, has been put.

The laboratory and the commercial methods for the generation of ozone differ from each other only in the size of the equipment and the quantities made. All ozone generators, though differing in mechanical details, depend on the principle that ozone is formed when a silent electrical discharge is passed through air, in which case the oxygen atoms rearrange themselves, as shown in the following equation:

$$3O_2=2O_3$$

This reaction, however, is reversible and, as mentioned above, if the ozone formed is not removed as fast as formed, it will immediately revert to oxygen.

$$2O_3=3O_2$$

The satisfactory technical production of ozone from air depends largely on the condition of the air, the best results being obtained when a dry, dense, cold air is used. The most

successful plants are, therefore, those that have a process of refrigeration for the air, before it is passed through the generator. Cooling to 0° C. gives excellent results, further cooling being unnecessary, for the maximum amount of ozone obtained from oxygen in air, 7.5 per cent., is obtained at 0° C.

45. Chemical Properties of Ozone.—The outstanding property of ozone is its great oxidizing power. It is a much more energetic oxidizing agent than oxygen. Many of the metals, including even those so difficult to oxidize as copper, mercury, and silver, are rapidly converted into oxides by ozone. One of its most characteristic effects is that on mercury this reaction is so delicate that a very small bubble of oxygen containing only $\frac{1}{50}$ of its bulk of ozone will destroy the luster of several pounds of mercury and cause the mercury to lose its mobility and the convexity of its surface. Some non-metals are at once oxidized by moist ozone. For example, phosphorus is oxidized to phosphoric acid, sulphur to sulphuric acid, sulphides to sulphates, and ferrocyanides to ferricyanides.

In aqueous solution, ozone sets iodine free from potassium iodide, as is shown by the formation of a blue color when starch is present. The following equation shows the change that takes place:

$$O_3+2KI+H_2O=O_2+2KOH+I_2$$

That is, 1 molecule of ozone reacts with 2 of potassium iodide and 1 of water to form 1 molecule of oxygen, 2 of potassium hydroxide, and 1 of iodine. Schönbein's test for ozone is based on this chemical change and is carried out by dipping a piece of filter paper into a starch emulsion containing a little potassium iodide, and then introducing the paper into the gas being tested. If ozone is present a deep-blue color will appear. This blue color is due to iodo-starch which is a solution of iodine in the solid starch that is suspended in water.

46. Schönbein's test, however, is not conclusive, since there are other elements and compounds such as chlorine, nitrogen peroxide, N_2O_2, and hydrogen peroxide, H_2O_2, which also lib-

erate iodine from potassium iodide. Therefore, unless it is known that these elements and compounds are not present, Schönbein's test is worthless, and in this case the action of ozone on silver is used as a test.

When a piece of silver foil is heated in the flame of a Bunsen burner for a moment and then while still warm, it is brought in contact with ozone or air containing ozone, the silver becomes black because of the formation of silver peroxide, Ag_2O_2.

$$2Ag+2O_3=Ag_2O_2+2O_2$$

47. Physical Properties of Ozone.—Ozone is a colorless gas having a penetrating odor not unlike that of chlorine. Its specific gravity is 1.658, or the gas is about 1.5 times as heavy as oxygen. Ozone is very unstable. It decomposes slowly at ordinary temperatures, but rapidly at high temperatures, and at 270° C., it cannot exist under ordinary conditions. At a pressure of 125 atmospheres and at −103° C., ozone becomes a dark-blue magnetic liquid which boils at −119° C. Ozone is not as soluble as oxygen in water, only 1 volume dissolving in 100 volumes of water at 12° C. It may be termed an allotropic modification of oxygen, the term being applicable when two or more forms result from the same element.

48. Uses for Ozone.—The commercial value of ozone depends on the fact that it can oxidize substances at a very low temperature, much lower than that at which oxygen does.

Ozone readily oxidizes organic matter. For example, it can destroy the organic odors that result from human and industrial activities and can change the nature of the disagreeable odors that prevail in meeting places, schools, glue factories, slaughter houses, chemical works, fertilizer plants, and many other establishments where disagreeable odors are generated. Ozone is, therefore, a valuable adjunct to ventilation systems.

Probably the most important of all uses for ozone is in the purification of water. Ozone, mixed with water by means of various mechanical devices, destroys the odor, unpleasant taste, and undesirable color of waters by oxidizing the organic bodies

that cause these objectionable properties. It also destroys the bacteria present. The gas is especially valuable for purification of water, because it is non-poisonous, leaves no taste, and is not absorbed by the water to any appreciable extent.

The industrial uses of ozone are constantly being increased. Tallows, fats, and oils can be made tasteless and odorless, and can be bleached and purified by the action of ozone. It is often found preferable to chlorine as a bleaching agent for various fabrics, because it is neither poisonous nor as objectionable to workmen as chlorine. It is used to some extent to convert linseed oil into varnish, and finds some application in the brewing industry to purify casks and water.

OXIDES OF HYDROGEN

WATER, OR HYDROGEN MONOXIDE

Formula H_2O. *Molecular weight 18.016. Specific gravity (water at 4° C.) 1.00. Boiling point (water) 100° C. Freezing point (water) 0° C.*

49. History.—Until 1776 water was considered an element, when Lavoisier proved its compound nature. Cavendish and Watt in 1781 proved its composition by synthesis, and in 1805 Humboldt and Gay-Lussac ascertained the ratio of its constituents by volume to be 1 : 2, while Berzelius and Dulong succeeded in proving its combining ratio by weight to be 1 : 8.

50. Occurrence.—Water occurs in nature as ice, snow, water, and steam. It is commonly observed in the form of springs, wells, rainfall, lakes, rivers, seas, and oceans; it constitutes a large part of all living bodies, and is found to some extent in minerals. It is the most abundant of all compounds and occurs in every part of the world.

Water, the liquid form in which condition hydrogen monoxide is most commonly found, seldom occurs in the pure state.

51. Chemical and Physical Properties of Water. Between the temperatures of 0° C. and 100° C., water is a

tasteless, limpid liquid, and when viewed in a moderate quantity is colorless. When seen in large masses it shows a distinct greenish-blue tint. It is neither acid nor alkaline in its action on vegetable colors; it is a poor conductor of heat and when perfectly pure is a non-conductor of electricity. It is almost incompressible, losing only 50 volumes in 1,000,000 volumes when the atmospheric pressure is doubled. Its most important property is its solvent power; there exist comparatively few substances that it does not dissolve in larger or smaller quantities. The oceans are the natural reservoirs from which our water supplies are drawn. By the heat of the sun immense quantities of sea-water are converted into vapor, which either remains suspended in the air or condenses and produces clouds. Special atmospheric conditions lead to the precipitation of this moisture as rain or snow. Rain and snow are the direct or indirect sources of spring and river water; these latter always contain more or less solid matter, depending on the condition of rock and soil over or through which they pass. The rivers always carry down to the ocean with them a certain proportion of solid matter, which precipitates when the water is again vaporized to form clouds. In this way a continuous though slow increase in the quantity of matter found in sea-water comes about. The constitution of sea-water naturally varies to a certain extent, according to locality and climate, but its principal constituents always are sodium chloride, magnesium compounds, and a number of other salts, of which iodides and bromides are the most important.

Water is a comparatively stable compound, as it is only slightly decomposed by the action of heat, the decomposition amounting to a little more than 1.0 per cent. at 1,875° C., and about 2.0 per cent. at 2,100° C. The products of decomposition are, of course, hydrogen and oxygen. Water unites with many oxides, either solid or gaseous, to form acids and bases, and with many salts to form hydrates.

52. Action of Water on Oxides.—The following equations illustrate the action of water on some of the commoner oxides:

(1)	CaO calcium oxide (quicklime)	+	H_2O	=	$Ca(OH)_2$ calcium hydroxide (slaked lime)
(2)	Na_2O sodium oxide	+	H_2O	=	$2NaOH$ sodium hydroxide
(3)	SO_2 sulphur dioxide	+	H_2O	=	H_2SO_3 sulphurous acid
(4)	P_2O_5 phosphorus pentoxide	+	$3H_2O$	=	$2H_3PO_4$ phosphoric acid

Equations (3) and (4) illustrate the meaning of the term anhydride as applied in chemistry. Thus, since the addition of water to the compounds sulphur dioxide and phosphorus pentoxide causes the formation of sulphurous acid and phosphoric acid, respectively, the oxides are termed the anhydrides of the acids. In other words, an **anhydride** is a substance which, when brought in contact with water, forms an acid. It should be remembered, however, that in this case the formation of an acid is not the result of a decomposition but results from the addition of water to the anhydride of the acid.

53. Hydrates.—The term hydrate is properly applied only to those compounds which contain combined water or water of crystallization, such as copper sulphate, $CuSO_4{\cdot}5H_2O$; ferrous sulphate, $FeSO_4{\cdot}7H_2O$; and barium chloride, $BaCl_2{\cdot}2H_2O$. Frequently, however, the hydroxides of the metals such as calcium hydroxide, $Ca(OH)_2$; sodium hydroxide, $NaOH$; and potassium hydroxide, KOH, are called hydrates, especially in commercial lines. True hydrates have a definite chemical composition and are not merely mixtures of salt and water, and they also possess physical properties which differ from water and the salts from which they have been prepared. Hydrates as a rule are unstable compounds; when heated, they lose water, the number of molecules of the latter driven off depending upon the degree of heat. When all the water has been driven off, the hydrate reverts to the anhydrous state. (The term *anhydrous* means *without water*.) Thus the hydrate, copper sulphate, $CuSO_4{\cdot}5H_2O$, becomes $CuSO_4$ and is called cupric sulphate. When hydrates are exposed to dry air for any length of time, they gradually lose their water of

crystallization and become an opaque white powder. On the other hand, some substances exist which absorb moisture from the atmosphere. Those which lose water are said to effloresce while the property of absorbing water is termed deliquescence.

54. Hygroscopic Water.—Water of crystallization should not be confused with water that is held in a substance mechanically as, for example, water in a sponge. In this case, the water is not a chemical part of the substance, but is merely mixed with it mechanically. The term hygroscopic water or hygroscopic moisture is applied to water that is mechanically mixed with a material.

At times some doubt may exist as to the manner in which the formula for a hydrate is written, but this may be logically dispelled by pointing out that since water is given up when a hydrate decomposes, it is only proper that the formula be written to show that the compound contains water, otherwise the formula for ferrous sulphate might just as well be written, $H_{14}FeSO_{11}$, which would show the same proportion by weight of each element but this formula would not show that the substance contained water nor would it indicate what might occur upon heating as does the conventional formula to a certain degree.

55. Molecular Weights of Substances Containing Water of Crystallization.—When calculating the molecular weights of a substance containing water of crystallization, the weight of the molecules of water must always be included, for the water of crystallization is considered a part of the substance. For example, calculate the molecular weight of hydrated cupric sulphate, $CuSO_4 \cdot 5H_2O$:

Atomic weight of copper is 63.57
Atomic weight of sulphur is 32.06
Atomic weight of oxygen is 16.00
Atomic weight of hydrogen is 1.008

There are 9 oxygen atoms, 10 hydrogen atoms, 1 sulphur atom, and 1 copper atom in the substance. Hence, the molecular weight is:

$$
\begin{array}{rl}
9 \times 16.00 & = 144.00 \text{ for oxygen} \\
10 \times 1.008 & = 10.08 \text{ for hydrogen} \\
1 \times 32.06 & = 32.06 \text{ for sulphur} \\
1 \times 63.57 & = \underline{63.57} \text{ for copper} \\
 & 249.71, \text{ the molecular weight of } CuSO_4{\cdot}5H_2O
\end{array}
$$

In solving problems into which the water of crystallization enters, the molecular weight of the substance containing the water may be calculated as in the foregoing case.

56. Natural Waters.—Water as has been previously stated is never met in an entirely pure state in nature. Whether it has rested on or has flowed over the surface of the soil; whether it has fallen in the form of dew, mist, or rain, or whether it has just emerged from underground, it always contains more or less solid matter in a state of suspension or of solution. The purest form of natural water is rainwater. Other natural waters may be divided into *potable,* or *drinkable, mineral,* and *saline waters.*

River and lake waters, especially such as are found in granite regions, are, as a rule, the purest. The water of Loch Katrine, in Scotland, for instance, does not contain more than 2 grains of solid matter to the gallon, and is one of the purest natural waters known. The following are the amounts of impurity in the water supplies of some of the large cities: That from Lake Cochituate, which furnishes the city of Boston with its water supply, contains only 3.11 grains of impurities to the gallon; the Schuylkill water, which supplies Philadelphia, contains 7.78 grains; the waters collected in the reservoirs of Ridgewood, for the supply of Brooklyn, 3.92 grains; the Croton water of New York City, 4.78; Lake Michigan, from which Chicago draws its water supply, 6.68 grains in every gallon. The water of the Thames which, to a great extent, supplies London, contains nearly 16.68 grains of impurities to each gallon.

Spring and well water, owing to the fact that they have, previous to their issue, penetrated the soil, are never as pure as surface waters. Thus, the water of a well near Central Park, New York City, showed 43.54 grains; one in Schenec-

tady, New York, 49.21 grains; one in Amsterdam, Holland, 69.93 grains; and one in London, England, 99.97 grains of solid matter to the gallon.

Mineral and saline waters are those which, by virtue of their chemical constituents or temperature, have a certain effect on the animal economy, and hence possess therapeutic properties.

They are either cold or warm; they are termed warm when they possess at the moment of their issue a temperature above 15° C. Their thermal state, of course, varies, covering the whole range of the thermometer from 15° C. to 100° C. There are numerous hot springs in Virginia, Colorado, and California. The temperature of the Grand Geyser in Iceland is far above 100° C.

57. According to their chemical constituents, mineral waters are classified in a number of characteristic groups, distinguished either by the predomination of certain constituents or by the presence of certain distinctly active components. These waters may be distinguished as follows:

Acidulous, or gaseous, waters, characterized by the presence of free carbon dioxide.

Alkaline waters, characterized by the presence of a larger or smaller proportion of sodium bicarbonate, or of an alkaline silicate, as well as common salt, and Glauber salt.

Chalybeate waters, characterized by holding an iron salt in solution.

Saline waters, or those which contain neutral salts, replacing the alkali bicarbonate.

Sulphur waters, characterized by the presence of hydrogen sulphide and other soluble sulphides.

Acidulous, or gaseous, waters are distinguished by the presence of free carbon dioxide, which is dissolved in the depth of the earth and under a pressure much greater than that of the atmosphere; hence, a certain portion of this gas becomes naturally disengaged as soon as the water emerges from the soil, thus creating more or less effervescence. Gaseous waters are cool, and their taste is pleasant at the moment of issue, but

sometimes these waters become saline, or even alkaline, after the disengagement of the greater proportion of their carbon dioxide. Natural gaseous waters never consist of a solution of carbon dioxide in pure water; they always contain a certain quantity of saline matters such as sodium, calcium, and magnesium carbonates, and sometimes even traces of chlorides and sulphates. Such is approximately the composition of certain of the Saratoga springs and the well-known Seltzer water.

Alkaline waters, as their name indicates, possess an alkaline reaction. This alkaline reaction is sometimes noticed immediately on their emergency, sometimes only after the loss of their free carbon dioxide. This reaction may be due to an alkaline silicate, but can generally be referred to as an alkaline carbonate. Acid sodium carbonate, or sodium bicarbonate, $NaHCO_3$, popularly known as bicarbonate of soda, is present in nearly all waters of this class. Vichy water, for instance, contains nearly 5 grams of this salt per liter.

Chalybeate waters are distinguished by holding more or less iron in solution, which gives to these waters an astringent taste and certain therapeutic properties. The traces of iron they contain may exist in three conditions: (1) As ferrous carbonate held in solution by carbonic acid. (2) As ferrous crenate. Berzelius gave the name of crenic acid to a body that is related to peculiar acids existing in the soil, and which are known as ulmic, humic, and geic acids. Ferrous crenate is soluble in water; its constitution, however, is unknown. (3) As ferrous sulphate. Hence, chalybeate waters may be carbonated, crenated, or sulphated.

58. Such waters, however, seldom contain ferrous salts in really considerable proportions; in fact, many ferruginous waters (that is, waters containing ferrous salts) of undoubted sanative power do not contain more than about 4 centigrams of these salts per liter. Through exposure to air they lose the greater portion of their carbon dioxide very soon, and ferrous carbonate is precipitated, which, in turn, soon loses its carbon dioxide and is converted into brown ferric hydroxide. Springs of chalybeate water frequently occur in this country as well

as in Europe. They exist in Bedford, Pennsylvania; Manitou, Colorado; Saratoga, New York; and many other places. The springs of Spa and Pyrmont, in Belgium; Bussang, in the Vosges; and Passy, near Paris, are known all the world over.

Saline water includes a great number of waters of various composition, charged with neutral salts, among which the most prominent are the chlorides, bromides, and iodides. According to the predominating or most active constituent, they are classified as chlorinated, sulphated, and bromoiodated waters.

Sea-water is a chlorinated water. It is a well-known fact that it contains a notable proportion of sodium chloride. This common salt is accompanied by the chlorides of potassium and magnesium and by a considerable amount of magnesium sulphate.

Sulphur water contains a soluble sulphide or hydrogen sulphide. This class of waters is divided into two distinct classes, namely, natural sulphur waters and accidental sulphur waters. The first class contains sodium sulphide, is hot when emerging from the soil, and contains little solid matter. The second class of waters embraces those that are formed on the spot by the reduction of sulphates, and particularly calcium sulphate, contained in the waters. This reduction is accomplished by the action of organic matters that impregnate the soil, and of which the combustible elements, carbon and hydrogen, remove the oxygen of the sulphates.

59. Effects of Heat on Water.—Among other properties of water, the physical changes it undergoes as a direct result of the application of heat are of such vast importance as to justify a somewhat extended description. It is a well-known fact that at a temperature below the freezing point water exists in the solid state. Every one is familiar with ice. Taking a piece of ice at a temperature considerably below that at which it was formed, say $-20°$ C., the following is a description of its changes as a result of the continuous application of heat:

As heat is first applied, the ice rises in temperature and at the same time increases in volume; these changes proceed

regularly until a temperature of 0° C. is attained. At that point the temperature remains stationary, notwithstanding the fact that the absorption of heat continues. During this time the ice melts, and the heat thus absorbed, without causing any corresponding elevation of temperature, is employed in converting the solid ice into liquid water. The heat necessary to melt a given quantity of ice at 0° C. into water at the same temperature would raise the same weight of water from 0° C. to 79° C., a fact that is expressed in other words by saying that the latent heat of water is 79 heat units. During the melting of ice a considerable diminution of volume occurs, only 10 volumes of water being produced by 10.9 volumes of ice. As soon as the whole of the ice is melted, the temperature once more begins to rise, and does so steadily until a temperature of 100° C. is attained. The water at 0° C. diminishes in volume with an increase in temperature, until at 4° C., when it commences to expand, and continues to do so until 100° C. is reached. At 4° C., therefore, water is at its maximum density; either a diminution or an increase of temperature will result in expansion. At 100° C. and the normal pressure of 760 millimeters the water begins to boil and remains stationary in temperature, but is not all at once converted into vapor; on the contrary, between five and six times as long is necessary to boil away the whole of the water as was needed to raise it from the freezing to the boiling point. Or, to express it in exact figures, the quantity of heat, the latent heat of steam, necessary to convert a given weight of water into steam, is sufficient to raise 536 times the same weight of water from 0° C. to 1° C. The steam produced is at the same temperature, 100° C., as the boiling water; this large amount of heat is employed in the conversion of water from the liquid to the gaseous state. The whole of the water having been converted into steam, a further application of heat results in the expansion of the steam, which follows the general laws governing the relation of gases to heat.

In cooling, steam passes through a series of changes that are just the converse to those that it undergoes on being heated. During the condensation of steam into water, and

the solidification of water to form ice, heat is liberated in the same quantity as was required in the first place to effect, respectively, the liquefaction of ice and the conversion of water into steam.

As has been previously stated, water is at its greatest density at 4° C.; and at this temperature 1 cubic centimeter of water weighs 1 gram; and above or below 4° C., 1 cubic centimeter weighs less than 1 gram. The extent of this variation in weight at different temperatures, is given by Table III.

TABLE III

VARIATION IN WEIGHT OF WATER AT DIFFERENT TEMPERATURES

Temperature	Gram	Temperature	Gram
0° C.	0.999868	15° C.	0.999126
1° C.	0.999927	20° C.	0.998230
2° C.	0.999968	25° C.	0.997071
3° C.	0.999992	30° C.	0.995673
4° C.	1.000000	40° C.	0.99224
5° C.	0.999992	50° C.	0.98807
6° C.	0.999968	60° C.	0.98324
7° C.	0.999929	70° C.	0.97781
8° C.	0.999876	80° C.	0.97183
9° C.	0.999808	90° C.	0.96534
10° C.	0.999727	100° C.	0.95838

From these figures, it will be readily seen why specific gravities must always be accompanied by the temperature at which they are taken.

60. As water is heated in a vessel or some other container, it becomes lighter and has a tendency to rise. This property is very important in steam boilers, for without it the water in boilers would not circulate properly and would render the boiler unsafe. As the water circulates in the boiler, it causes an equal distribution of heat throughout every part of the apparatus, and thereby prevents accidents due to unequal expansion

of any parts. Hence, it is apparent that the present design of steam boilers is due to the fact that water when heated expands, becomes lighter, and rises.

61. The Effect of Pressure on the Boiling Points of Liquids.—It has been found that water boils at 100° C. when the pressure exerted on it is 760 millimeters and that a higher temperature is needed to boil water when the pressure is greater than 760 millimeters and a lower temperature when it is less than 760 millimeters. The principle that the higher

TABLE IV

BOILING POINT OF WATER AT DIFFERENT PRESSURES

Boiling Point Degrees C.	Pressure Millimeters	Boiling Point Degrees C.	Pressure Millimeters
100.4	771.95	99.4	743.83
100.3	768.20	99.3	741.16
100.2	765.46	99.2	738.50
100.1	762.73	99.1	735.85
100.0	760.00	99.0	733.21
99.9	757.28	98.9	730.58
99.8	754.57	98.8	727.96
99.7	751.87	98.7	725.35
99.6	749.18	98.6	722.75
99.5	746.50	98.5	720.15

the pressure exerted on a liquid, the higher is its boiling point and the lower the pressure on the liquid, the lower is its boiling point applies to all liquids. Table IV shows some determinations that clearly illustrate this principle.

62. Pressure of Aqueous Vapor.—The tendency of a liquid to vaporize results in a pressure opposing that of the atmosphere. This pressure is known as the vapor pressure of the liquid. In the case of water, it is called the pressure of aqueous vapor. Before a liquid can boil, its vapor pressure must exceed the pressure exerted on the liquid. The

greater the temperature of a liquid, the greater is its vapor pressure. Therefore, to increase the pressure of aqueous vapor, it is simply necessary to heat the water; to boil water, it is necessary only to increase its temperature until its vapor pressure is equal to the pressure exerted on it, normally 760 millimeters. Table IV shows that the temperature of the water must be 100° C. To give another illustration, suppose that the pressure exerted on the water is 720.15 millimeters. According to Table IV the temperature of the water must be raised to 98.5° C. before the vapor pressure can equalize the pressure exerted on the water. Hence, Table IV shows not only the boiling points of water under various pressures but gives the pressure of aqueous vapor at different temperatures.

From the foregoing facts, it is apparent that a liquid boils when its vapor pressure equals that of the pressure exerted on it. To obtain this condition, one must either increase the vapor pressure by raising the temperature of the liquid or reduce the pressure exerted on the liquid, by withdrawing the air from an enclosed space above the liquid. Ordinary distillation is a familiar example of the first method and distillation in vacuo is an illustration of the second. Both are used extensively in industrial operations, the first where heat does not affect the process and the second where the substances to be distilled are decomposed by temperatures at which they normally boil.

63. Water as a Solvent.—Water can be mixed with a great many gases, liquids, and solids to form clear, transparent, homogeneous liquids. (The term transparent is applied to bodies through which objects can be seen; the term homogeneous to materials that are the same throughout.) The addition of a teaspoonful of common table salt to a quart of water forms a liquid that is apparently but one substance, for there is nothing to show that two substances are present and the salt does not separate from the water, if allowed to stand any length of time. The mixture of salt and water is termed an aqueous solution of salt; the salt, called the *solute*, is dissolved in water, called the *solvent*.

64. Water is the most generally used of all solvents, for it can dissolve many substances of various kinds without materially affecting the chemical properties of those substances. It is often used as a solvent to accelerate or produce chemical changes by bringing substances into more intimate contact with each other. For example, ordinary baking powders usually contain alum, and either a phosphate or a tartrate. This mixture will stand unchanged in the dry state indefinitely. As soon as water is added, however, chemical action takes place, as shown by the liberation of a gas. Water is instrumental in

TABLE V

SOLUBILITIES OF SOME SUBSTANCES IN WATER

One Part by Weight	Parts by Weight	
	Cold Water	Hot Water
Ammonium chloride	3.4	1.37
Barium nitrate	12.50	3.11
Boric acid	51.3 (0° C.)	2.94
Bromine	30.0	31.9 (30° C.)
Mercuric chloride	15.22	1.85
Sodium borate	21.5	1.82

producing chemical changes in innumerable operations such as the one here mentioned.

From the discussion in the previous paragraph, it is apparent that many substances that are chemically inactive in the dry state, react readily when in solution. This fact is worth remembering, for its applications both in the laboratory and in the manufacturing plant are practically unlimited.

65. The question naturally arises as to how much of a substance a definite amount of water can dissolve. Materials like grain alcohol can dissolve in water in any proportion, but the amounts of other substances are limited. Temperature is an important factor in determining the amount of matter that

can be dissolved by water, when that substance is soluble in water only up to a certain point.

Table V shows that a smaller quantity of hot water than of cold water is generally needed to dissolve a fixed amount of a substance; in other words, a substance will usually dissolve to a greater extent in hot water than in cold. There are exceptions to this rule, as, for example, bromine. The table shows that less bromine is dissolved in hot water than in cold.

Gases are usually less soluble in hot than in cold water, and solids are less soluble in cold than in hot water. Therefore, keeping the solvent cool hastens solution when the solute is a

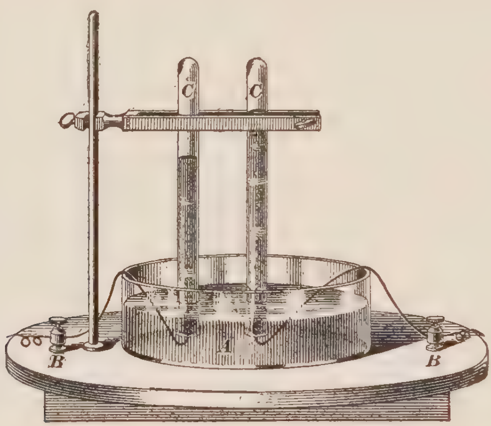


FIG. 11

gas and heating a solvent hastens solution when the solute is a solid or liquid.

66. The Composition of Water by Volume.—The decomposition of water into its constituents, hydrogen and oxygen, is carried out most conveniently and accurately by means of an electric current. A typical form of apparatus for this purpose is shown in Fig. 11, which consists of a shallow glass basin *A*, containing water to which a little sulphuric acid has been added (acidulated water), and two electrodes connected to the binding screws *B*, *B*. The glass tubes *C*, *C* are also filled with acidulated water, and each is inverted over one

of the electrodes. The battery wires are connected to the binding screws *B, B,* to which the electrodes have been attached. As soon as this connection has been made, it will be noticed that gas immediately begins to rise in each of the tubes, and it will be further noticed that in the tube inverted over the negative electrode the volume is double that evolved from the positive electrode. When the tube containing the larger quantity of gas, that is, the one over the negative electrode, is nearly full, it is removed, and a light applied to its mouth; the collected gas burns quietly, with the familiar blue flame of hydrogen. If a glowing match is plunged into the second tube of gas, it immediately bursts into flame, thus proving that the gas is oxygen. This experiment proves that water may be decomposed into its component parts, namely hydrogen and oxygen, and, furthermore, that these components exist in water in the proportion of 2 to 1.

Fig. 12

If pure water were used for electrolysis it would not conduct the current and consequently there would be no action; therefore, water containing an acid or an alkali must be used.

67. It has already been shown in Art. **14,** that the reunion of oxygen and hydrogen again produces water.

The recombination of hydrogen and oxygen may also be effected with the aid of the electric spark, which is passed through a mixture of these gases. Cavendish in his investigations made use of a strong glass vessel with two platinum wires inserted in it so that the electric spark might pass through the gases between their ends, as shown in Fig. 12. *A* represents the glass vessel, which, after being exhausted by an air pump, is attached to a graduated glass jar *B* containing a mixture of 2 volumes of hydrogen and 1 volume of oxygen. On opening the stop-cock *C* the vessel fills with the mixture of gases. The stop-cock is again closed and an electric spark is flashed through this mixture; drops of water will be noticed on the sides of the vessel. This operation may be repeated a number of times, until the whole of the gases have been caused to combine; by this time there will be an appreciable quantity of water in the glass vessel.

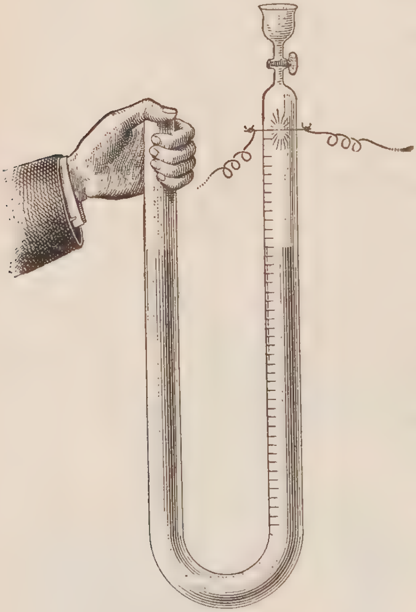


FIG. 13

68. For the purpose of measuring exactly the proportions in which hydrogen and oxygen unite, an instrument called a eudiometer is employed.

Fig. 13 represents a form of this apparatus proposed by Ure. It consists simply of a **U**-shaped tube of glass which is closed at one end, the closed limb being graduated, and it has two platinum wires fused near its extremity. This limb is to be filled with water and then a given quantity of pure oxygen —20 cubic centimeters, for instance, is to be introduced from a delivery tube; 50 cubic centimeters of pure hydrogen is then

similarly introduced, all measurements being made when the level of the liquid is the same in both limbs. The open end is closed firmly by the thumb, as represented in the drawing, a cushion of air being left between it and the liquid, and an electric spark is passed through the mixture of hydrogen and oxygen by means of the platinum wires. Upon restoring the level of the liquid by adding water, 10 cubic centimeters of gas will be left which on examination will be found to be pure hydrogen. Hence, 20 volumes of oxygen has united with 40 volumes of hydrogen to form water, which is the ratio 1 : 2, required by theory and which is expressed by the formula H_2O.

69. Composition of Water by Weight.—The preceding experiments have shown the composition of water by volume; but it is necessary to become acquainted with the means employed for the determination of the exact composition of water by weight. The synthesis by weight cannot be effected with accuracy by weighing the gases themselves, on account of their large volume. It is therefore accomplished by passing an indefinite quantity of hydrogen over a known weight of pure, hot oxide of copper, when hydrogen combines with the oxygen of the oxide to form water, according to the equation:

$$\underset{\text{copper oxide}}{CuO} + \underset{\text{hydrogen}}{H_2} = \underset{\text{water}}{H_2O} + \underset{\text{copper}}{Cu}$$

The loss of weight from the oxide of copper gives the amount of oxygen; and, if this is deducted from the weight of the water, the weight of hydrogen will be ascertained.

The apparatus employed for this purpose is represented in Fig. 14.

70. The apparatus shown in Fig. 14 consists of a generating bottle *A*, in which hydrogen is evolved by the action of zinc and sulphuric acid. To this is attached a wash bottle *B*, partly filled with a solution of potassium hydroxide, in order to retain any traces of sulphuric acid that may be carried over mechanically by the evolved hydrogen. To this wash bottle are attached by means of leading tubes and stoppers, three

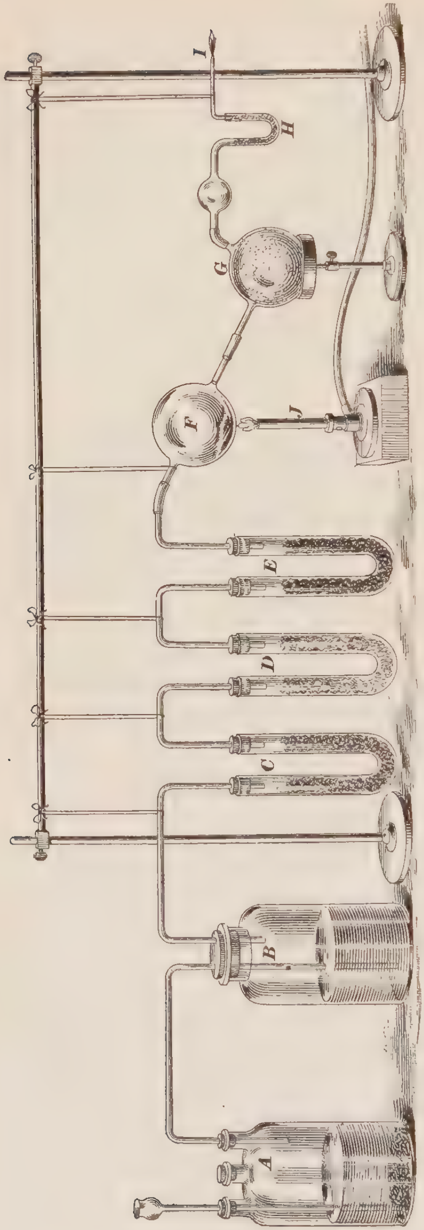


Fig. 14

U-shaped tubes *C*, *D*, and *E*. The tube *C* contains pumice moistened with a solution of mercuric chloride to absorb any hydrogen sulphide; the tube *D* contains fragments of fused potassium hydroxide, which removes any carbon dioxide; and the tube *E* contains pumice moistened with strong sulphuric acid to dry the hydrogen. The object of the wash bottle and these three tubes is to remove all impurities from the evolved hydrogen, thus allowing only perfectly pure and dry hydrogen to pass into the bulb *F*. This bulb, or globe *F*, consists of a blown piece of combustion tubing which is attached to *E* by a piece of rubber tubing, and is in such a position that a Bunsen burner may be placed underneath it. The bulb *G* also connected with *F* by a short piece of rubber

tubing, is used for the collection of water, and is in turn connected with a drying tube *H*, filled with small pieces of calcium chloride.

Having this apparatus so far in readiness, about 20 grams of perfectly dry copper oxide is placed in the bulb *F* and both are accurately weighed together. Then *G* and *H* are weighed separately and the apparatus reconnected, being very careful to make all joints perfectly air-tight.

By the addition of a small quantity of sulphuric acid to the generating bottle *A* through the funnel tube, in order to cause a slow evolution of hydrogen, the hydrogen passing through the entire outfit expels the air from it; as soon as pure hydrogen emerges from the jet *I*, the copper oxide in the bulb *F* is slowly heated by means of the Bunsen burner *J*. It will soon be noticed that water is produced and that it collects in receiver *G* any traces of vapor being retained by the calcium chloride in *H*. After about 10 minutes, the burner *J* is removed and the bulb *F* allowed to cool. As soon as this bulb has thoroughly cooled, the apparatus is disconnected; the generating bottle *A* is first removed and air drawn through the tubes by blowing into the glass tubing leading into the wash bottle *B*, so as to displace all hydrogen; then the copper-oxide globe *F* is disconnected and carefully weighed; the loss in weight represents the oxygen that has combined with hydrogen to form water. Bulb *G* and drying tube *H* are again weighed; their combined increase in weight is the water that has been produced.

71. Suppose, as the result of an actual experiment, that the copper oxide, which was placed in the bulb *F*, had lost 15.88 grams of oxygen, and that the receiver *G* and drying tube *H*, which contains small pieces of anhydrous calcium chloride, were found to have gained 17.88 grams in weight. We therefore would know that water contains 15.88 parts by weight of oxygen and 2 parts by weight of hydrogen in 17.88 parts of it, or 7.94 parts by weight of oxygen to 1 part by weight of hydrogen. This is a simple but typical experiment which illustrates the fact that what has previously been known only as a theory is actually based on sound principles.

TABLE VI

SPECIFIC GRAVITY OF WATER AT TEMPERATURES FROM 0° C. TO 102° C.

Temp. Deg. C.	Specific Gravity	Temp. Deg. C.	Specific Gravity	Temp. Deg. C.	Specific Gravity
0	0.99987	35	0.99406	70	0.97781
1	.99993	36	.99371	71	.97723
2	.99997	37	.99336	72	.97666
3	.99999	38	.99299	73	.97607
4	1.00000	39	.99262	74	.97548
5	.99999	40	.99224	75	.97489
6	.99997	41	.99186	76	.97428
7	.99993	42	.99147	77	.97368
8	.99988	43	.99107	78	.97307
9	.99981	44	.99066	79	.97245
10	.99973	45	.99024	80	.97183
11	.99963	46	.98982	81	.97120
12	.99952	47	.98940	82	.97057
13	.99940	48	.98896	83	.96994
14	.99927	49	.98852	84	.96930
15	.99913	50	.98807	85	.96865
16	.99897	51	.98762	86	.96800
17	.99880	52	.98715	87	.96734
18	.99862	53	.98669	88	.96668
19	.99843	54	.98621	89	.96601
20	.99823	55	.98573	90	.96534
21	.99802	56	.98524	91	.96467
22	.99780	57	.98478	92	.96399
23	.99756	58	.98425	93	.96330
24	.99732	59	.98375	94	.96261
25	.99707	60	.98324	95	.96192
26	.99681	61	.98272	96	.96122
27	.99654	62	.98220	97	.96051
28	.99626	63	.98167	98	.95981
29	.99597	64	.98113	99	.95909
30	.99567	65	.98059	100	.95838
31	.99537	66	.98005	101	.95765
32	.99505	67	.97950	102	.95693
33	.99473	68	.97894		
34	.99440	69	.97838		
35	.99406	70	.97781		

Tables VI, VII, and VIII are to be used for reference purposes only.

TABLE VII

WEIGHT OF 1 GALLON OF WATER

Temp. Deg. C.	Grams	Pounds	Temp. Deg. C.	Grams	Pounds
0	3780.520	8.33461	50	6.20	.2369
1	0.758	.33613	51	4.50	.2332
2	0.930	.33551	52	2.72	.2292
3	1.037	.33575	53	0.98	.2254
4	1.082	.33585	54	3729.16	.2214
5	1.067	.33582	55	7.35	.2174
6	0.992	.33565	56	5.50	.2133
7	0.861	.33536	57	3.76	.2095
8	0.675	.33495	58	1.75	.2051
9	0.435	.33442	59	3719.86	.2009
10	0.144	.33378	60	7.93	.1966
11	3779.798	.33302	61	5.97	.1923
12	9.403	.33215	62	4.00	.1880
13	8.960	.33117	63	2.00	.1835
14	8.472	.33009	64	3709.95	.1790
15	7.939	.32892	65	7.91	.1745
16	7.362	.32765	66	5.87	.1700
17	6.741	.32628	67	3.79	.1655
18	6.080	.32482	68	1.67	.1608
19	5.375	.32327	69	3699.56	.1561
20	4.630	.32162	70	7.40	.1514
21	3.845	.31989	71	5.21	.1465
22	3.021	.31808	72	3.05	.1418
23	2.157	.31617	73	0.82	.1369
24	1.256	.31419	74	3688.59	.1319
25	0.317	.31212	75	6.36	.1270
26	3769.341	.30996	76	4.05	.1219
27	8.329	.30773	77	1.78	.1169
28	7.283	.30543	78	3679.48	.1119
29	6.201	.30304	79	7.13	.1067
30	5.086	.30058	80	4.79	.1015
31	3.938	.29805	81	2.41	.0963
32	2.757	.29545	82	0.02	.0910
33	1.545	.29278	83	3667.64	.0858
34	0.301	.29003	84	5.22	.0804
35	3759.027	.28723	85	2.76	.0750
36	7.725	.28436	86	0.31	.0696
37	6.393	.28142	87	3657.81	.0641
38	5.033	.27842	88	5.31	.0586
39	3.645	.27536	89	2.78	.0530
40	2.232	.27225	90	0.25	.0474
41	0.53	.2685	91	3647.71	.0418
42	3749.05	.2652	92	5.14	.0362
43	7.54	.2619	93	2.53	.0304
44	5.99	.2585	94	3639.92	.0247
45	3744.40	8.2550	95	7.32	.0189
46	2.81	.2515	96	4.67	.0131
47	1.23	.2480	97	1.98	.0072
48	3739.56	.2443	98	3629.34	.0018
49	7.90	.2407	99	6.61	7.9953
			100	3.93	.9894

TABLE VIII

WEIGHT OF 1 CUBIC FOOT OF WATER

Temp. Deg. C.	Grams	Pounds	Temp. Deg. C.	Grams	Pounds
0	28280.254	62.3472	50	48.69	.616
1	82.033	.3511	51	35.96	.588
2	83.321	.3540	52	22.67	.559
3	84.121	.3557	53	09.65	.530
4	84.458	.3565	54	27896.08	.500
5	84.345	.3562	55	82.50	.470
6	83.784	.3550	56	68.64	.440
7	82.804	.3528	57	55.63	.411
8	81.413	.3498	58	40.63	.378
9	79.618	.3458	59	26.49	.347
10	77.441	.3410	60	12.06	.315
11	74.853	.3353	61	27797.36	.283
12	71.898	.3288	62	82.65	.250
13	68.584	.3215	63	67.66	.217
14	64.933	.3134	64	52.38	.184
15	60.946	.3046	65	37.11	.150
16	56.630	.2951	66	21.83	.116
17	51.985	.2849	67	06.27	.082
18	47.040	.2740	68	27690.44	.047
19	41.766	.2624	69	74.59	.012
20	36.193	.2501	70	58.47	60.976
21	30.321	.2371	71	42.07	.940
22	24.157	.2235	72	25.95	.905
23	17.694	.2093	73	09.25	.868
24	10.954	.1944	74	27592.57	.831
25	03.930	.1789	75	75.88	.794
26	28196.629	.1629	76	58.62	.756
27	89.059	.1462	77	41.65	.719
28	81.234	.1289	78	24.39	.681
29	73.140	.1111	79	06.86	.642
30	64.799	.0927	80	27489.32	.604
31	56.212	.0737	81	71.50	.564
32	47.377	.0543	82	53.68	.525
33	38.311	.0343	83	35.86	.486
34	29.005	.0138	84	17.76	.446
35	19.475	61.9926	85	27399.37	.405
36	09.735	.9713	86	80.99	.365
37	28099.771	.9493	87	62.31	.324
38	89.596	.9269	88	43.65	.282
39	79.215	.9040	89	24.70	.241
40	68.645	.8807	90	05.74	.199
41	55.90	.853	91	27286.80	.157
42	44.86	.828	92	67.56	.115
43	33.55	.803	93	48.05	.072
44	21.94	.778	94	28.52	.029
45	28010.06	61.752	95	09.01	59.986
46	27998.19	.725	96	27189.20	.942
47	86.31	.699	97	69.13	.898
48	73.86	.672	98	49.33	.854
49	61.42	.644	99	28.96	.809
			100	08.87	.765

HYDROGEN PEROXIDE

Formula, H_2O_2. Molecular weight 34.016

72. History and Occurrence.—Hydrogen peroxide or hydrogen dioxide was discovered in 1818 by Thenard, who called it *oxygenated water.*

The extent to which hydrogen peroxide occurs in nature has long been a disputed point, but it is probable that it is present in very small quantities in rain, snow, and in the air. Many of the tests made to show that hydrogen peroxide does exist in the atmosphere, etc., also give the same results with ozone and other oxidizing substances, resulting in uncertainty concerning its occurrence in nature.

73. Laboratory Preparation.—Hydrogen peroxide can be made on a small scale by adding sodium peroxide, Na_2O_2, a little at a time, to a weak solution of hydrochloric acid, in which case the following change takes place:

$$Na_2O_2+2HCl=H_2O_2+2NaCl$$

The mixture of hydrogen peroxide, sodium chloride, and water (water is introduced in the hydrochloric-acid solution and takes no direct part in the chemical change) is thoroughly and repeatedly shaken with ether. Upon standing, the mixture separates into layers, the solution of hydrogen peroxide and water in ether rising to the top and the salt and part of the water settling to the bottom. The ethereal solution of water and hydrogen peroxide, after being drawn off, is distilled at a low temperature (about 45° C.) to evaporate the ether from the mixture, thereby leaving an aqueous solution of hydrogen peroxide.

Hydrogen dioxide can also be made by shaking crystalline barium dioxide, $BaO_2 \cdot 8H_2O$, in a weak solution of cold sulphuric acid, during which operation the following reaction takes place:

$$BaO_2 \cdot 8H_2O+H_2SO_4=BaSO_4+H_2O_2+8H_2O$$

Pure hydrogen peroxide is separated from the barium sulphate and water mixture by distilling under reduced pressure.

74. Technical Production of Hydrogen Peroxide. Hydrogen peroxide is made on a commercial scale by decomposing barium dioxide with sulphuric acid or phosphoric acid. The equations representing the reactions which take place, depending upon the acid used, may be written as follows:

$$BaO_2+H_2SO_4=BaSO_4+H_2O_2$$
$$3BaO_2+2H_3PO_4=Ba_3(PO_4)_2+3H_2O_2$$

75. A mixture of barium dioxide and water, about the thickness of cream, is prepared and then added slowly to the cold acid, the temperature being kept below 15° C. After the proper amount, determined by experience, has been added, the precipitate of barium sulphate or barium phosphate, depending on whether sulphuric acid or phosphoric acid has been used, is allowed to settle. The clear liquid containing hydrogen peroxide and a little excess of acid, is then poured off. The slight excess of acid is allowed to remain in the solution of hydrogen peroxide, because it has been found that the substance is more stable in an acid than in an alkaline or in a neutral (neither alkaline nor acid) solution. The mixture of water and hydrogen peroxide can be further separated by distilling in vacuo, as previously described. Phosphoric acid is often given the preference over sulphuric acid in the foregoing process, because it precipitates impurities, such as iron and manganese contained in the barium dioxide, and thereby produces a purer product than does sulphuric acid, which chemical does not remove these impurities.

Hydrogen peroxide can also be manufactured by the action of hydrofluoric acid on barium dioxide in lead-lined tanks. The tanks are lead lined to prevent chemical action between hydrofluoric acid and the metal, usually iron, from which the tanks are made, for lead is not readily acted on by hydrofluoric acid. The mixture of the acid and the dioxide is stirred continuously and kept at as low a temperature as possible, for it has been found that best results are obtained under these conditions. The reaction, which is complete in about 12 hours, is shown by the equation:

$$BaO_2+2HF=BaF_2+H_2O_2$$

The clear liquid is drawn off after the insoluble barium fluoride has settled. The barium fluoride is treated with sulphuric acid to recover hydrofluoric acid which can be used again. The following reaction takes place during this recovery operation:

$$BaF_2+H_2SO_4=BaSO_4+2HF$$

The insoluble barium sulphate is separated from the hydrofluoric acid by decantation.

76. Chemical Properties of Hydrogen Peroxide. Chemically hydrogen peroxide is an extremely active compound, and this property is due to the fact that upon decomposition each molecule of the compound gives up one atom of oxygen (nascent oxygen) even at low temperatures. It is fairly stable in dilute aqueous solutions, especially when small amounts of free acid are present. Alkalies and salts have a tendency to hasten the decomposition of the substance. It has been found that the addition of certain substances tends to prevent the decomposition of hydrogen peroxide. For example, the organic substance acetanilide is used in commercial peroxide, for even as small an amount as one-half of 1 per cent. will increase the stability of the solution to such an extent that less than 3 per cent. will decompose in ½ year. Light also has a tendency to hasten the decomposition of hydrogen peroxide. For this reason the commercial product is generally sold in dark-colored bottles. Finely divided metals such as silver and platinum cause the substance to decompose rapidly. These metals act as catalytic agents and take no direct part in the reaction, as shown in the equation:

$$2H_2O_2=2H_2O+O_2$$

In solution hydrogen peroxide acts as a feeble acid, for it turns blue litmus red and reacts with some substances in a manner similar to that of acids; thus strontium hydroxide reacts with hydrogen peroxide to replace the hydrogen atoms in hydrogen peroxide with strontium, as follows:

$$Sr(OH)_2+H_2O_2=SrO_2+2H_2O$$

and an acid, like sulphuric acid, reacts in a like manner:

$$Sr(OH)_2+H_2SO_4=SrSO_4+2H_2O$$

In this instance, the strontium replaces the hydrogen atoms in the sulphuric acid.

77. The most prominent chemical characteristic of hydrogen peroxide is its power to supply oxygen readily; that is, its power as an oxidizing agent. It is even more active than oxygen, O_2, in this respect, for it liberates oxygen in the nascent state, O, as shown in the equation $H_2O_2 = H_2O + O$, in which condition it is very active. It can liberate iodine from hydrogen iodide; thus:

$$2HI + H_2O_2 = 2H_2O + I_2$$

Two molecules of hydrogen iodide react with 1 molecule of hydrogen peroxide to produce 2 molecules of hydrogen monoxide, or water, and 1 molecule of iodine.

Hydrogen peroxide can convert sulphides into sulphates, as shown in the equation:

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O$$

One molecule of lead sulphide is oxidized by 4 molecules of hydrogen peroxide into 1 molecule of lead sulphate; 4 molecules of hydrogen monoxide, or water, are also produced.

It is an excellent oxidizing agent for many organic compounds. In the case of dyes, it oxidizes them, changes their chemical nature, and, therefore, destroys their color. A dye retains its color only as long as its chemical composition remains unaffected.

Hydrogen peroxide can, under certain conditions, act as a *reducing agent;* that is, as an agency for the removal of oxygen from a compound. Thus, silver oxide is reduced by hydrogen peroxide to silver:

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2$$

78. Physical Properties of Hydrogen Peroxide. Pure hydrogen peroxide is a syrupy liquid having a specific gravity of about 1.5. It can be cooled to a solid that melts at −2° C., and can be boiled at 85° C., when the pressure exerted upon it is reduced to 68 millimeters. It is soluble in both water and alcohol in all proportions. Pure hydrogen

peroxide in contact with the skin causes blistering. The dilute, aqueous solution has a bitter metallic taste.

79. Uses of Hydrogen Peroxide.—Substances that react chemically with coloring matter to form either colorless or lighter-hued products are called bleaching agents. Hydrogen peroxide, owing to its power to oxidize organic coloring matter to lighter-colored substances, is used as a bleaching agent and is applied to delicate materials such as straw, feathers, hair, ivory, and silk, that are liable to be damaged by stronger bleaches. A mixture of sodium peroxide, acid, and water, which substances react to produce hydrogen peroxide, as has already been explained, is often used for this purpose under the name soda bleach.

Blackened paintings, containing lead colors, are often restored to their original tints by hydrogen peroxide. The black color is due to lead sulphide formed by the action of hydrogen sulphide, often found in the air of cities, on the lead compounds in the painting. Hydrogen peroxide oxidizes the black lead sulphide to the light-hued lead sulphate.

Hydrogen peroxide is used very largely in surgical, medicinal, and hygienic work, for it readily liberates nascent oxygen, an agent that kills bacteria, prevents infection, and improves hygienic conditions. It probably prevents infection by destroying the organisms causing tissue decomposition and by oxidizing the intermediate products of decomposition.

Hydrogen peroxide is sold in solutions of various strengths, the most common of which are 3 per cent. and 30 per cent. The strength of a hydrogen peroxide solution is also expressed in terms of the volume of oxygen liberated from a unit volume (100 cubic centimeters) of solution. For example, a solution marked 10 volumes can liberate 10 cubic centimeters of oxygen gas from 100 cubic centimeters of solution. A 3 per cent. solution evolves about 10 volumes of oxygen from every volume of solution.

INORGANIC CHEMISTRY
(PART 5)

NITROGEN AND CARBON AND THEIR COMPOUNDS

NITROGEN

PROPERTIES, PREPARATION, AND COMPOUNDS

Symbol N. Atomic weight 14.008. Molecular weight 28.016.

1. History.—Nitrogen was discovered in 1772 by Rutherford, a professor of botany in the University of Edinburgh, who showed that air after it had been breathed by an animal and washed with lime water, contained a gas that would support neither respiration nor combustion. Scheele and Lavoisier soon afterwards found independently of each other, that this substance constituted four-fifths of the air, by volume. Lavoisier recognized it to be an element and called it *azote* (from the Greek word, meaning *without life*), because it did not support life. The English name indicates that it is a constituent of saltpeter, KNO_3, the Latin name for which is *nitrum*.

2. Occurrence.—As already stated, air consists of approximately four-fifths nitrogen, but aside from this source, nitrogen is found in many forms of combination with oxygen and metals, such as potassium and sodium. Nitrogen is also an essential constituent of many vegetable and animal substances.

3. Laboratory Preparation.—Practically pure nitrogen may be made by subjecting air to the action of hot metallic

copper. When air is passed over red-hot copper turnings contained in a tube furnace, the oxygen of the air quickly combines with the copper, forming copper oxide,

$$2Cu + O_2 = 2CuO$$

leaving the nitrogen. Iron acts in a similar manner.

The easiest method of preparing pure nitrogen is to heat ammonium nitrite. The reaction goes as follows:

$$NH_4NO_2 + \text{heat} = 2H_2O + N_2$$

Ammonium nitrite, however, is a very unstable compound and cannot be easily kept, so, in practice, strong solutions of ammonium chloride, NH_4Cl, and sodium nitrite, $NaNO_2$, are mixed, the reaction taking place as follows:

$$NH_4Cl + NaNO_2 = NH_4NO_2 + NaCl$$

and when heat is applied, the ammonium nitrite breaks up, setting nitrogen free.

4. There are various other methods of preparing nitrogen, all of which are interesting from a theoretical point of view. For instance, the gas is evolved by passing chlorine into an excess of ammonia. The hydrogen and chlorine unite, and nitrogen is liberated:

$$\underset{\text{ammonia}}{2NH_3} + \underset{\text{chlorine}}{3Cl_2} = \underset{\substack{\text{hydrochloric}\\\text{acid}}}{6HCl} + \underset{\text{nitrogen}}{N_2}$$

A secondary reaction goes on between the acid formed and the excess of ammonia, thus:

$$\underset{\text{ammonia}}{6NH_3} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{6HCl} = \underset{\substack{\text{ammonium}\\\text{chloride}}}{6NH_4Cl}$$

These two reactions may be expressed by one equation:

$$\underset{\text{chlorine}}{3Cl_2} + \underset{\text{ammonia}}{8NH_3} = \underset{\substack{\text{ammonium}\\\text{chloride}}}{6NH_4Cl} + \underset{\text{nitrogen}}{N_2}$$

If a solution of ammonia or of an ammonium salt is treated with an alkaline solution of sodium hypobromite, nitrogen is evolved, thus:

$$\underset{\text{ammonia}}{2NH_3} + \underset{\substack{\text{sodium}\\\text{hypobromite}}}{3NaOBr} = \underset{\substack{\text{sodium}\\\text{bromide}}}{3NaBr} + \underset{\text{water}}{3H_2O} + \underset{\text{nitrogen}}{N_2}$$

This nitrogen is obtained in a perfectly pure condition by passing it through dilute sulphuric acid and dilute caustic soda and then passing it over heated copper and copper oxide.

5. Chemical Properties.—Nitrogen in a free state is a remarkably inert body, combining directly with only a very small number of elements at ordinary temperatures. However, if nitrogen is passed through a tube over strongly heated calcium, magnesium, or lithium, the nitrides of these elements are formed. They have the formulas, Ca_3N_2, Mg_3N_2, and Li_3N, respectively. Nitrogen combines with difficulty with hydrogen to form ammonia, and with still greater difficulty with oxygen to form nitric oxide, NO; but, although the gas is very inert, the compounds that it does form are among the most energetic known.

Thus, the corrosive nitric acid, HNO_3, the pungent ammonia, NH_3, the explosive nitroglycerine, $C_3H_5(NO_3)_3$, and even such an active poison as prussic acid, HCN, as well as numerous alkaloids, all contain more or less nitrogen.

6. Physical Properties.—Nitrogen is a colorless, odorless, and tasteless gas; it is lighter than air, its specific gravity being .967. It extinguishes burning bodies and is not itself combustible. Nitrogen may be liquefied at a temperature of $-146°$ C., and a pressure of 35 atmospheres; at atmospheric pressure, the liquid nitrogen boils at $-195.5°$ C. The gas is soluble to the extent of 2.3 volumes in 100 volumes of water at 0° C.

7. Uses of Nitrogen.—Nitrogen is used in the so-called nitrogen lamp in which the filaments of the lamp become white-hot in an atmosphere of nitrogen and because of the great chemical inactivity of this gas they are not attacked and the lamp burns with great brilliancy. Nitrogen is also used in high-temperature thermometers, the space above the mercury being filled with the gas, and as the mercury expands under the influence of high temperatures the nitrogen column is compressed, the pressure exerted upon the mercury preventing its boiling.

THE ATMOSPHERE

A gaseous mixture. Specific gravity 1

8. Occurrence.—The aerial envelope that surrounds the earth and is of vital importance to all beings that live and breathe in it, is called the *atmosphere*. Its existence is demonstrated whenever it is set in motion, as then we have winds, which, when sufficiently violent, produce well-known physical effects.

9. Properties.—Careful experiments have shown that, among other properties of matter, the atmosphere possesses weight. Regnault has shown that air, which has been chosen as the standard of specific gravity for gases, is 14.43 times heavier than hydrogen. Torricelli showed in 1643 that the pressure of the air on the earth's surface would sustain a column of mercury about 76 centimeters in height; and as a column of mercury of this height with an area of 1 square centimeter weighs 1,033 grams, it follows that this number represents the atmospheric pressure on every square centimeter of the earth's surface.

10. Composition.—The atmosphere consists chiefly of a mixture of nitrogen with $\frac{1}{5}$ volume of oxygen. In addition to these two elements, there are also present varying quantities of aqueous vapor, carbon dioxide, ammonia, nitric acid, and traces of argon, neon, helium, krypton, and xenon. The average composition of the atmosphere is approximately as shown in Table I.

TABLE I

Oxygen	20.61 parts
Nitrogen, argon, etc.	77.95 parts
Carbon dioxide	.04 part
Aqueous vapor	1.40 parts
Nitric acid Ammonia Methane Hydrogen sulphide Sulphur dioxide, etc.	Traces, according to the location—whether city, village, seashore, etc.

Although the proportion of oxygen in the air at a given spot may be diminished and that of carbon dioxide increased

by processes of oxidation (such as respiration and combustion) taking place there, the operations of wind and diffusion so rapidly mix the altered air with the greater general mass of the atmosphere that the variations in the composition of air in different places are very slight.

11. The composition of the atmosphere is generally expressed in terms of the quantity of oxygen and nitrogen contained in it, argon and nitrogen usually being classed as nitrogen. In determining these elements, care must be taken to exclude any errors due to the presence of carbon dioxide, ammonia, aqueous vapor, etc. The composition of the atmosphere is determined by means of the apparatus shown in Fig. 1. This apparatus was devised by Dumas and Boussingault.

The air is passed through the **U** tubes *A*, which are filled with potassium hydroxide to remove any carbon dioxide, then through the **U** tubes *B* containing sulphuric acid, which removes the water and ammonia. The air is now passed through the tube *C*, which is filled with metallic copper and placed in a furnace so that it can be heated to redness. The globe *D* and the tube *C* are exhausted by means of an air pump, and are accurately weighed. The apparatus is connected, the tube *C* is heated to redness, the stop-cocks *E* and E_1 are opened to allow the air to pass slowly through the apparatus. The air in passing through the tube *C* has all the oxygen removed by its absorption by the heated copper, and only the nitrogen passes over in the globe *D*. After a quantity of air has passed through *C* the stop-cocks are closed and after cooling the globe and tube are weighed. The weight of the tube is the weight of the oxygen plus some nitrogen, and the weight of the globe represents a part of the nitrogen. The tube is exhausted, the nitrogen it contained being withdrawn and again weighed. The difference in these latter weights of the tube is added to the weight of nitrogen in the globe, and the difference between the first and last weights of the tube represents the oxygen in the air.

12. Air a Mixture.—The fact that air is a mixture and not a chemical compound may be proved in numerous ways.

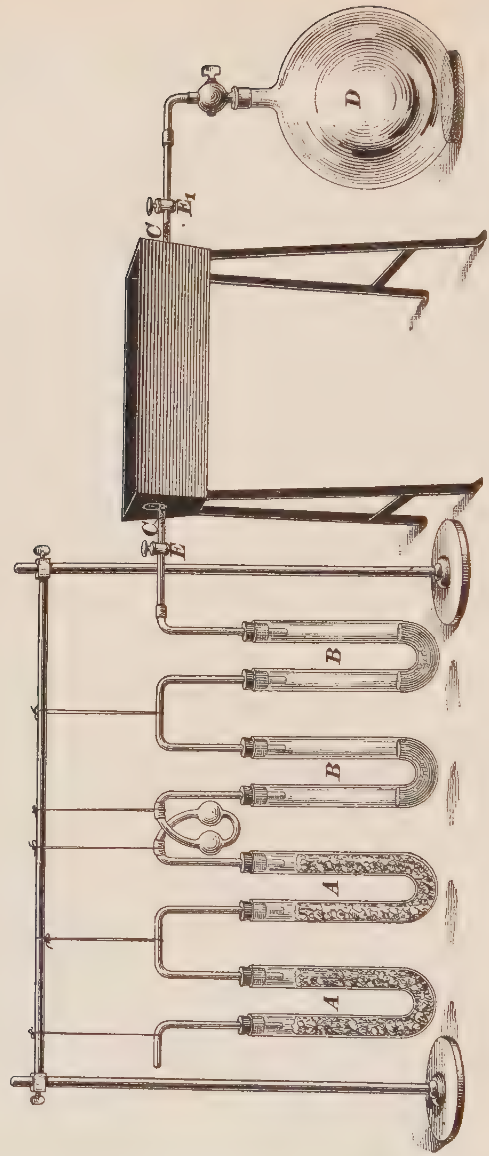


Fig. 1

In the first place, the oxygen and nitrogen are not present in any simple multiple of their atomic weights, which is necessary in all chemical compounds. Air differs also greatly from all compounds of these two elements which are known to chemistry. If a mixture is made of nitrogen and oxygen in the proportion in which they exist in air, it will be found that no alteration of volume takes place and that there is no increase of temperature; the mixture simply exhibits all the properties of ordinary atmospheric air.

The most conclusive evidence that these gases are mixed and not combined is that they may be separated by the action of water as a solvent. Oxygen is much more soluble than nitrogen, and if water that has been freed from gases by boiling is shaken with air and again boiled, the expelled gas is found, on analysis, to be much richer in oxygen than was the air, the oxygen amounting to about 34 per cent. of the dissolved gas.

As previously described, air can be separated into its chief components, oxygen and nitrogen, by liquefying it and then allowing the more volatile nitrogen to evaporate. Obviously then, if air were a chemical compound it would boil at a constant temperature and it would not be possible to separate it into its components by a simple distillation.

13. Rare Elements in the Air.—Lord Rayleigh has shown that 1 liter of nitrogen prepared by removing the oxygen of air weighs 1.2572 grams, whereas a liter of nitrogen prepared chemically weighs 1.2506 grams. This would indicate that there is in the air some substance heavier than nitrogen that remains with the nitrogen. This led Lord Rayleigh and W. Ramsey to investigate the composition of the air, when they discovered that it contains at least five previously unknown substances, which are present in the following proportions:

Argon,	1 volume	in	100 volumes of air
Neon,	$1\frac{1}{2}$ volumes	in	100,000 volumes of air
Krypton,	1 volume	in	20,000,000 volumes of air
Xenon,	1 volume	in	170,000,000 volumes of air
Helium,	1 volume	in	250,000 volumes of air

HELIUM

Symbol He. Atomic weight, 4.00

14. History.—On the 18th of August, 1868, P. J. C. Janssen discovered by the use of a spectroscope during an eclipse, a bright yellow line in the atmosphere of the sun. Frankland and Lockyer called this line D_3, and since no substance previously discovered on the earth showed the same line in the spectrum, it was ascribed to a hypothetical element which they called helium from the Greek word *helios,* meaning the sun.

In the year 1889, W. F. Hillebrand, of the United States Geological Survey, reported that he had obtained about 2.5 per cent. of a peculiar gas by treating the mineral uraninite with inorganic acids. This gas in some respects was similar to nitrogen, yet in others it was totally different from ordinary nitrogen.

Sir William Ramsay some time later repeated Hillebrand's experiments and also obtained the peculiar gas described by the latter, and in the spectrum of this gas with the aid of Sir William Crookes he found a line corresponding to that of Janssen, thus proving the existence of a new element to which the name helium was given. In 1895 the characteristic line of this gas was found in the spectrum of the atmosphere by Kayser, and Travers and Ramsay actually obtained the element from the air in the same year.

15. Occurrence.—Helium occurs widely distributed in nature but in small quantities, it being found in air to the extent of 1 volume in 250,000 volumes of the latter. As previously mentioned, helium is also found in certain mineral substances and in the gases given forth by volcanoes. The largest source of helium at present is, however, the natural gas of this country, some of the gas produced by the wells in the states of Oklahoma, Texas, Ohio, and Kansas containing as much as 2.5 per cent. of the element.

16. Properties.—Helium is a monatomic gas and is classed with the rare elements of the atmosphere, namely argon, neon, krypton, and xenon. It is an inert gas and cannot be

ignited or exploded, and these properties, combined with its great lifting power, led to extensive research work in an effort to produce the gas in large quantities so that it might be used in balloons instead of the inflammable hydrogen.

Helium, next to hydrogen, is the lightest substance known, its specific gravity being .1368 as compared with .06949 for hydrogen. Thus, helium is almost twice as heavy as hydrogen. The gas has a critical temperature of about −268° C.; and a critical pressure of 2.75 atmospheres. It is slightly soluble in water, about 1.4 cubic centimeters dissolving in 100 cubic centimeters of water at 0.5° C. Upon rapidly evaporating liquid helium a temperature of −270.5° C., almost absolute zero, has been reached. Helium in the solid form, however, has not yet been obtained. Liquid helium is colorless and mobile, has a specific gravity of .122 and is therefore one of the lightest liquids known. It boils at −268.5° C.

The buoyant effect exerted by helium is equivalent to 92.6 per cent. of that exerted by hydrogen. It has been determined that 1,000 cubic feet of pure hydrogen will lift a weight of 75.14 pounds and a like amount of pure helium will lift 69.58 pounds, while 1,000 cubic feet of a mixture consisting of 85 per cent. helium and 15 per cent. hydrogen, which is the mixture contemplated for general aircraft use, will have 93.4 per cent. of the lifting power of pure hydrogen and will lift 70.18 pounds.

17. Production.—Up to April, 1918, helium was more or less of a chemical curiosity, as only about 100 cubic feet had been produced, on a laboratory scale, at a cost of from $1,700 to $2,000 a cubic foot, since its discovery.

In the process of producing fairly pure helium in large quantities as practiced in this country during the year 1918, natural gas containing from .4 per cent. to 1.0 per cent. helium is subjected to a high pressure and simultaneous cooling. In this manner the methane, CH_4, is liquefied (−82.8° C.; at 45.6 atmospheres) while helium remains in the gaseous state, and a more or less complete separation is thus effected.

Helium was first produced on a large scale in this country at plants located at Fort Worth, Texas, which worked on gas supplied by a pipe-line from Petrolia, in the same state. These plants produced a gas containing about 92.5 per cent. helium which was stored in steel cylinders at a pressure of 2,000 pounds per square inch, ready to be used.

COMPOUNDS OF NITROGEN AND HYDROGEN

AMMONIA

Formula NH_3. *Molecular weight 17.032*

18. History.—Gaseous ammonia was discovered by Priestley in 1774, when he collected the gas evolved by the action of lime on *sal ammoniac*, NH_4Cl. Priestley named the gas alkaline air. An ammoniacal liquid, called spirits of hartshorn, was also obtained by the destructive distillation of the hoofs and horns of animals.

19. Occurrence.—Ammonia exists in the free state in small quantities in the air and in rainwater. It is generally a post-mortem product, as dead animal and vegetable matter yields it in putrefaction. The urine and excrement of animals contain refuse nitrogenous matter that on being exposed to the air is changed into ammonia and in this way causes these substances to be such valuable fertilizers, as most plants are incapable of assimilating nitrogen in a free state but are able to do so when that element is presented to them as ammonia.

The compounds of ammonia are found in beds of guano (the excrement of sea fowl) on certain ocean islands. The most important of these compounds, ammonium chloride, also called sal ammoniac, was first obtained from Egypt. The name ammonia is said to be derived from that of Jupiter Ammon, owing to the circumstance that the Arabs extracted one of the compounds of ammonia from the dung of camels near a temple dedicated to this god. Quills, horn, hair, etc. heated in a closed vessel evolve a number of gases, among which is

ammonia. Coal contains about 2 per cent. of nitrogen, and in its destructive distillation for the manufacture of gas, ammonium compounds are always obtained.

20. Laboratory Preparation.—Ammonia may be prepared from any of the ammoniacal salts by heating with a strong base such as calcium hydroxide or sodium hydroxide. Of these, calcium hydroxide is used most on account of its cheapness. If, ammonium chloride and calcium hydroxide are heated together, the following reaction occurs:

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O$$

In order to decompose thoroughly the ammonium chloride, about 2 parts of calcium hydroxide are used to 1 part of the ammonium chloride.

The most convenient method, however, of obtaining gaseous ammonia in the laboratory is to heat gently strong ammonium hydroxide, NH_4OH, in a retort or in a distilling flask.

21. Commercial Manufacture.—An industrial method for the production of ammonia results from the manufacture of illuminating gas and coke in by-product coke ovens. In this process, the gases that are given off during the dry distillation of coal are passed through water, which dissolves out the ammonia. The ammonia liquor is then heated with milk of lime, $Ca(OH)_2$, and the escaping ammonia is led into concentrated sulphuric acid. In this way crystallized ammonium sulphate is obtained. Thus,

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

After recrystallization, the ammonium sulphate is again distilled with milk of lime,

$$(NH_4)_2SO_4 + Ca(OH)_2 = 2NH_3 + CaSO_4 + 2H_2O$$

and the ammonia set free is either liquefied and run into steel cylinders for future use or it may be absorbed in water,

$$NH_3 + H_2O = NH_4OH$$

and sold as the ammonium hydroxide or aqua ammonia of commerce.

22. Synthetic Ammonia.—The building up of a chemical compound from the elements of which it is composed is

called **chemical synthesis,** the result being a synthetic compound as distinguished from the naturally occurring compound. Thus, we have seen how ammonia can be recovered from natural sources, and in the following process a method is outlined showing how ammonia can be synthesized directly from the elements nitrogen and hydrogen.

23. Haber Process.—It has long been a matter of common knowledge among chemists that nitrogen and hydrogen could be made to combine to form ammonia if mixtures of these gases were subjected to the action of an electric spark, but it has been within recent years that a process has been developed by which nitrogen and hydrogen are made to combine at comparatively low temperatures by passing a mixture of the gases over a suitable catalytic agent.

Details of the Haber process, named after its inventor, are lacking, but it is essentially as follows: A mixture of the pure gases is passed through the apparatus over the catalyst, which is said to consist of specially prepared iron, at a temperature of about 500° C.; and under a pressure of 175 to 200 atmospheres. The extent of combination of the gases is not very great, but the ammonia formed is either liquefied or absorbed in water and the uncombined gases are sent through the apparatus again so that there is no loss.

24. Manufacture of Ammonia, Cyanamide, and Calcium Carbide.—The following description serves to show the order of formation and methods of manufacture of three valuable commercial products, namely: Ammonia, cyanamide, and calcium carbide.

Calcium carbide is made by strongly heating lime and carbon in an electric furnace,

$$CaO+3C=CaC_2+CO$$

After grinding, the calcium carbide is charged into an electric furnace of special design, where it is kept at a temperature of 1,000° C. Pure, dry nitrogen is then passed over the hot calcium carbide, the following reaction taking place:

$$CaC_2+N_2=CaCN_2+C$$

The resulting product, calcium cyanamide, $CaCN_2$, is next treated with water to remove any lime and then with oil to render it dustless and it is sold under the name cyanamide. This product is now extensively used in the manufacture of fertilizers.

Upon treating cyanamide with steam, ammonia is evolved,

$$CaCN_2+3H_2O\ (\text{steam})=CaCO_3+2NH_3$$

25. Chemical Properties of Ammonia.—Ammonia is often called a volatile alkali.

Its characteristic property is that it combines directly with acids to form salts. Thus,

$$\underset{\text{ammonia}}{NH_3} + \underset{\text{hydrochloric acid}}{HCl} = \underset{\text{ammonium chloride}}{NH_4Cl}$$

$$\underset{\text{ammonia}}{NH_3} + \underset{\text{nitric acid}}{HNO_3} = \underset{\text{ammonium nitrate}}{NH_4NO_3}$$

$$\underset{\text{ammonia}}{2NH_3} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{ammonium sulphate}}{(NH_4)_2SO_4}$$

The group NH_4 is one of the best and most striking examples of a compound radical; it behaves in so many compounds as if it were an element that it has received the name ammonium. It cannot, however, be isolated, for it immediately decomposes into ammonia and free hydrogen. Ammonia does not burn in air, but does in oxygen, water, and nitrogen, traces of ammonium nitrite, NH_4NO_2, and nitrogen dioxide, NO_2, being formed. A mixture of ammonia and oxygen explodes violently when ignited. Or,

$$20NH_3+19O_2=22H_2O+4N_2+4NH_4NO_2+4NO_2$$

Chlorine gas takes fire when passed into ammonia, nitrogen, and hydrochloric acid, HCl, being formed.

$$2NH_3+3Cl_2=N_2+6HCl$$

The latter unites with the remaining ammonia to form ammonium chloride. The hydrogen of ammonia is replaceable by metals. Magnesium burns in ammonia, forming magnesium nitride, Mg_3N_2. Or,

$$4NH_3+6Mg+3O_2=2Mg_3N_2+6H_2O$$

When ammonia is conducted over hot sodium or potassium, sodium amide, $NaNH_2$, or potassium amide, KNH_2, is formed, respectively. Or,

$$2NH_3+2Na=2NaNH_2+H_2$$

26. Physical Properties of Ammonia.—At ordinary temperatures, ammonia is a gas possessing a characteristic odor. It is poisonous when breathed in large quantities. The gas is much lighter than air, having a specific gravity of .5971. It may be easily liquefied, its critical temperature being 132.3° C., and the critical pressure 109.6 atmospheres. Liquid ammonia boils at −38.5° C., and may be frozen to a solid, which melts at −77.3° C. The gas is extremely soluble in water, 1 volume of the latter dissolving 1,049.6 volumes of ammonia at 0° C., and 727.2 volumes of the gas at 15° C.

The per cent. of ammonia in a water or aqueous solution may be quickly determined by means of the specific gravity of the solution. The higher the specific gravity is the lower the per cent. of ammonia in the solution. Table II gives the per cent. of ammonia in solutions of varying specific gravity.

TABLE II

STRENGTH OF AMMONIA SOLUTIONS

Specific Gravity 15.6° C.	Per Cent. NH_3	Specific Gravity 15.6° C.	Per Cent. NH_3
.8805	35.28	.9412	15.37
.8946	30.38	.9589	10.28
.9106	24.99	.9790	5.02
.9256	20.16	.9947	1.21

27. Uses of Ammonia.—Because of the great amount of heat absorbed by liquid ammonia upon evaporation, it is extensively used as a refrigerating agent. The importance of gaseous ammonia lies in the fact that it unites directly with acids to form salts. Thus, the valuable fertilizer, ammonium sulphate, is made by passing the gas into sulphuric acid. Sal ammoniac or ammonium chloride is used in the manufacture

of different types of wet batteries. The solution of the gas in water, or ammonium hydroxide, has many household uses. Ammonium nitrate is used in the manufacture of explosives.

HYDRAZINE AND HYDROXYLAMINE

28. For many years, ammonia was the only known compound of nitrogen with hydrogen. Lately, two others have been discovered, namely, hydrazine, N_2H_4, and hydroxylamine, NH_2OH, both of which are very closely related to ammonia.

Hydrazine, N_2H_4, is prepared according to the following reactions: The action of sodium hypochlorite, $NaOCl$, on ammonia yields chloramine,

$$NH_3+NaOCl=NH_2Cl+NaOH$$

Chloramine then reacts with ammonia to form hydrazine hydrochloride,

$$NH_2Cl+NH_3=NH_2{\cdot}NH_2HCl$$

In order that a large yield of hydrazine hydrochloride be obtained, the presence of a small quantity of glue or albumin is necessary. Its action, however, is at present unknown.

To prepare pure hydrazine, the solution of the hydrochloride is evaporated to expel excess ammonia and then treated with HCl, whereupon the pure hydrazine hydrochloride, $NH_2{\cdot}NH_2{\cdot}HCl$, separates in crystals. When this salt is distilled with a strong solution of potassium hydroxide under reduced pressure, a solution of hydrazine hydrate, $N_2H_4{\cdot}H_2O$, is formed,

$$NH_2{\cdot}NH_2{\cdot}HCl+KOH=KCl+N_2H_4{\cdot}H_2O$$

And the hydrazine hydrate may be isolated by fractional distillation. Hydrazine may be prepared by distilling this hydrate with barium oxide, BaO, under reduced pressure.

$$N_2H_4{\cdot}H_2O+BaO=N_2H_4+Ba(OH)_2$$

Hydrazine is a fuming liquid, which boils at 113.5° C., and unites with water with the evolution of heat to form the hydrate. Like ammonia, it unites with acids directly to form salts.

29. Hydroxylamine, NH_2OH, derives its name from the fact that it consists of an *amino* group, NH_2, united with an hydroxyl group. Hydroxylamine is formed by the action of hydrochloric acid containing a little dilute nitric acid, upon tin. As has been previously stated, when hydrochloric acid reacts with tin, nascent hydrogen is evolved.

$$Sn+2HCl=SnCl_2+2H$$

and this nascent hydrogen reduces nitric acid, and hydroxylamine is formed,

$$HNO_3+6H=NH_2OH+2H_2O$$

Some of the hydroxylamine thus formed is further reduced by the hydrogen, to ammonia,

$$NH_2OH+2H=NH_3+H_2O$$

and since HCl is present in the solution, ammonium chloride and hydroxylamine hydrochloride, $NH_2OH{\cdot}HCl$, are also formed.

Stannous chloride, $SnCl_2$, is now removed from the solution by passing hydrogen sulphide gas through it, stannous sulphide, SnS, being precipitated,

$$SnCl_2+H_2S=SnS+2HCl$$

The stannous sulphide is filtered off and after evaporating the filtrate to dryness the residue is treated with alcohol which dissolves the hydroxylamine hydrochloride but not the ammonium chloride. The hydroxylamine hydrochloride upon treatment with a solution of sodium hydroxide gives hydroxylamine.

$$NH_2OH{\cdot}HCl+NaOH=NH_2OH+NaCl+H_2O$$

Pure crystals of hydroxylamine melt at 33° C., the compound gradually decomposes when heated above 15° C., at normal pressure and when heated at higher temperatures it decomposes with explosive violence. Hydroxylamine is used to a great extent as a reducing agent in the synthesis of organic compounds.

30. Hydrazoic acid, N_3H, may be prepared by passing nitrous oxide, N_2O, over sodamide at a temperature of about 200° C.

$$N_2O+NH_2Na=N_3Na+H_2O$$

Sodium azoimide, N_3Na, is first formed as is indicated by the equation and the free acid, N_3H, is then obtained by distilling the sodium azoimide with dilute sulphuric acid.

$$2N_3Na + H_2SO_4 = 2N_3H + Na_2SO_4$$

Pure hydrazoic acid is a liquid with a penetrating odor; it boils at 37° C., and is extremely explosive even in a water solution. Metallic salts of the acid are also very explosive and extremely dangerous to handle. The lead salt, $Pb(N_3)_2$, called lead azide, lead azoimide, or lead hydrazoate, is now being used as a substitute for mercury fulminate as a detonator for explosives.

COMPOUNDS OF NITROGEN WITH CHLORINE AND IODINE

31. When chlorine gas is passed into a warm, concentrated solution of ammonium chloride, nitrogen trichloride separates as a heavy oily liquid.

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl$$

Nitrogen trichloride has a specific gravity of 1.653. It explodes at 95° C. when heated.

Nitrogen iodide, $N_2H_3I_3$, is formed when an alcoholic solution of iodine is added to a solution of ammonium hydroxide. The reaction proceeds as follows, ammonium hypoiodite, NH_4IO, being first formed:

$$I_2 + 2NH_4OH = NH_4IO + NH_4I + H_2O$$

This compound then decomposes, giving nitrogen iodide,

$$3NH_4IO = N_2H_3I_3 + NH_4OH + 2H_2O$$

When it is made according to the above directions, nitrogen iodide separates in the form of reddish-brown crystals, which are extremely explosive when dry, but which may be safely handled when moist.

OXIDES AND ACIDS OF NITROGEN

32. There are five oxides and three oxygen acids of nitrogen. The following arrangement illustrates the system according to which they are named:

Oxides	Acids	Sodium Salts
Nitrous oxide, N_2O	Hyponitrous acid, $H_2N_2O_2$	Sodium hyponitrite, $Na_2N_2O_2$
Nitric oxide, NO		
Nitrogen trioxide, N_2O_3	Nitrous acid, HNO_2	Sodium nitrite, $NaNO_2$
Nitrogen tetroxide, N_2O_4, or dioxide, NO_2		
Nitrogen pentoxide, N_2O_5	Nitric acid, HNO_3	Sodium nitrate, $NaNO_3$

By far the most important of the oxygen acids of nitrogen is nitric acid, because of the fact that the other oxides and acids may be either directly or indirectly obtained from it and because of the great number of uses to which it has been put in chemical industries. For these reasons, it is proper that a discussion of its preparation and properties should take precedence over others.

NITRIC ACID

Formula HNO_3. Molecular weight 63.016

33. History and Occurrence.—Nitric acid was known to Geber, an alchemist, who lived in the 8th century; Raymond Lully in 1225 described a method of preparing it; and in 1785 Cavendish thoroughly investigated this compound and determined its composition synthetically. It exists in small quantities in the atmosphere, from which it is separated by rain, which, consequently, usually exhibits, on analysis, traces of this acid. The salts of nitric acid, with sodium and potassium (sodium and potassium nitrates), are its most common sources.

Layers of potassium nitrate are found incrusting the soil in India, and of sodium nitrate in parts of Peru and Chile. These nitrates are produced by the oxidation of nitrogenous organic matter in the presence of the bases potassium and sodium hydroxides. Potassium nitrate is also known as saltpeter, or niter; sodium nitrate is frequently called *Chile* saltpeter, or cubic niter, from the shape of its crystals.

34. Preparation.—Nitric acid is always produced by the distillation of a nitrate—generally sodium or potassium nitrate—with sulphuric acid. The two are mixed in a retort, and on the application of heat (about 100° C.), nitric acid, being volatile, distils over, leaving acid sodium sulphate or sodium hydrogen sulphate. The reaction may be represented thus:

$$\underset{\text{sodium nitrate}}{NaNO_3} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{nitric acid}}{HNO_3} + \underset{\text{acid sodium sulphate}}{NaHSO_4}$$

If two molecules of sodium nitrate are used to one of sulphuric acid and the temperature is increased, the resulting acid sulphate is decomposed as follows:

$$NaHSO_4+NaNO_3=Na_2SO_4+HNO_3$$

The temperature required for this reaction frequently decomposes a part of the nitric acid formed.

The reaction which takes place at the higher temperature (above 100° C.) may be represented by one equation:

$$2NaNO_3+H_2SO_4=Na_2SO_4+2HNO_3$$

For the purpose of carrying out the preparation of nitric acid in the laboratory, the quantities of materials used may be molecular, that is, 1 gram-molecule of sulphuric acid may be mixed with 1 gram-molecule of sodium nitrate and the mixture heated, but since reactions do not always go to completion, greater yields of product are obtained by using an excess of one of the reacting substances. In this case sulphuric acid is the cheaper material, therefore an excess of it (about 10 per cent.) is used. The arrangement of apparatus for the work is illustrated in Fig. 2.

35. Commercial Manufacture of Nitric Acid.—In the manufacture of nitric acid on a large scale, the process is essentially that used in the laboratory, the same reactions taking place. On the manufacturing scale, however, the materials entering into the construction of the plant and the precautions taken to insure economy of operation, differ radically from those used in the laboratory. The stills used in plant operation are constructed of cast iron, the condensers are made up of earthenware pipes and the nitric acid is collected in earthenware jars. Some plants operate under reduced pressure which

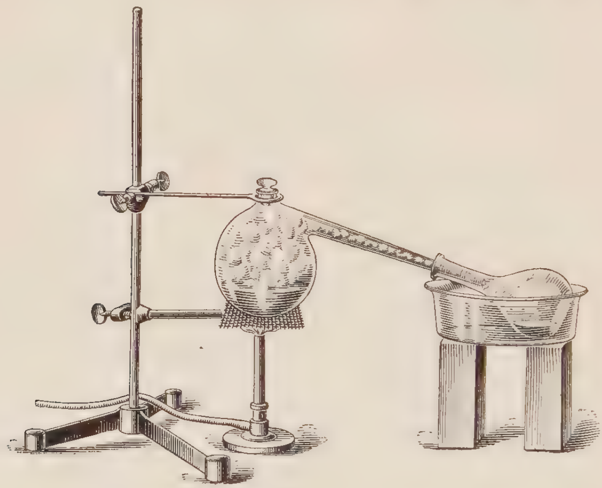


FIG. 2

makes distillation at a lower temperature possible, thus avoiding, to a certain extent, decomposition of the nitric acid formed into lower oxides of nitrogen which will subsequently be discussed. By this means leaks are also prevented, since if in any part of the system a crack should develop through which the gases are passing, air will be drawn in, but nitric acid and the oxides of nitrogen present will not escape.

36. Fixation of Nitrogen.—As has been stated, nitrogen is a very inert gas and ordinarily does not enter into chemical combination with other elements or substances. In the Birkeland-Eyde process, however, for the manufacture of nitric

acid from atmospheric nitrogen, the nitrogen of the air is caused to combine with oxygen by passing air through an electric arc. The temperature of this arc is from 2,500° C. to 3,000° C., and the product of the reaction between nitrogen and oxygen is nitric oxide, NO, about 1.0 per cent. being formed. This gas, after passing the arc, is quickly cooled so as to permit the reaction between it and additional oxygen to take place,

$$2NO+O_2=2NO_2$$

The product in this case, nitrogen dioxide or tetroxide, decomposes at about 150° C. After oxidation of the nitric oxide, the mixture of air and nitrogen dioxide is passed into the bottom of vertical towers which are packed with acid-proof stoneware over which water trickles, and the nitrogen dioxide, coming in contact with this water, forms nitric acid,

$$3NO_2+H_2O=2HNO_3+NO$$

The nitric oxide set free as shown by the equation combines with additional atmospheric oxygen to form nitrogen dioxide, which is again passed through the tower. This cycle is constantly repeated and none of the oxides of nitrogen are wasted.

37. Chemical Properties of Nitric Acid.—Pure nitric acid is an unstable compound; at ordinary temperatures it is decomposed by sunlight, becoming yellow in color because of the presence of the lower oxides of nitrogen produced by its partial decomposition. The pure acid may be made by distilling the less concentrated acid of commerce with sulphuric acid under reduced pressure.

Chemically, nitric acid is a powerful oxidizing agent, all the common metals being attacked by it, nitrates being formed. Gold and platinum, however, are not affected by it. Nitric acid is monobasic and forms normal salts only, which may be represented by the general formula $M(NO_3)_x$, in which M may represent any metal or group and x indicates the number of NO_3 radicals, as, for instance, in the compounds barium nitrate, $Ba(NO_3)_2$, or ferric nitrate, $Fe(NO_3)_3$.

The action of nitric acid on the metals is generally more complex than the action of hydrochloric or sulphuric acid. It first oxidizes the metal, a portion of the acid being reduced, liberating one or more of the lower oxides of nitrogen. The remaining nitric acid dissolves the oxide of the metal, forming a nitrate and water. The particular oxide evolved, and the proportions of each present in a mixture, depend on the metal used, the temperature at which the reaction takes places, the degree of concentration of the acid, and various other causes.

Thus, when dilute nitric acid acts on metallic copper, the nitrate of the metal and nitric oxide, NO, are formed,

$$3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO$$

and when the concentrated acid acts on copper, the following reaction takes place,

$$Cu+4HNO_3=Cu(NO_3)_2+2H_2O+2NO_2$$

The action of dilute nitric acid on zinc produces nitrous oxide and not nitric oxide as in the case of copper,

$$4Zn+10HNO_3=4Zn(NO_3)_2+N_2O+5H_2O$$

while with the concentrated acid, the reaction is

$$4Zn+9HNO_3=4Zn(NO_3)_2+NH_3+3H_2O$$

No general rule can, therefore, be given which will govern the writing of equations representing such reactions as these, but it must be remembered that conditions of temperature and the concentration of the acid used in an oxidizing action determine to a great extent the products which will be formed.

The salts of nitric acid are known as nitrates, and these may be prepared either by the action of the acid on the metal, as with copper or zinc, or by treating an oxide or a carbonate with the acid.

The nitrates, like the acid from which they are derived, are powerful oxidizing agents; potassium nitrate is used as a source of oxygen in black gunpowders, or blasting powders which are mixtures, of that compound with sulphur and charcoal.

If charcoal is dropped into melted potassium nitrate it takes fire and burns with great brilliancy.

Nitric acid and all the nitrates are decomposed at red heat, the metallic oxides remaining, while oxygen and the oxides of nitrogen are driven off. A good example of this is given in the reaction that takes place when nitric acid is passed through a red-hot tube of clay.

$$\underset{\text{nitric acid}}{4HNO_3} = \underset{\text{water}}{2H_2O} + \underset{\text{nitrogen peroxide}}{4NO_2} + \underset{\text{oxygen}}{O_2}$$

or, when potassium nitrate is heated to 400° C., the following change occurs:

$$\underset{\text{potassium nitrate}}{2KNO_3} = \underset{\text{potassium nitrite}}{2KNO_2} + \underset{\text{oxygen}}{O_2}$$

38. Aqua Regia.—Neither nitric acid nor hydrochloric acid alone has the property of dissolving gold; but a mixture of 1 volume of concentrated nitric and 3 volumes of concentrated hydrochloric acid, to which mixture the name *aqua regia* has been given, readily attacks the metal. This property of dissolving gold depends on the presence of chlorine, which is liberated in the action of the acids on each other, as shown in the equation:

$$HNO_3+3HCl=2H_2O+NOCl+Cl_2$$

39. Fuming Nitric Acid.—Fuming nitric acid is brown in color by reason of the large quantity of nitrogen tetroxide which it contains. It may be prepared by distilling ordinary nitric acid with a little starch.

40. Physical Properties of Nitric Acid.—Pure nitric acid is a colorless, fuming, corrosive liquid. Cooled to −41.3° C., the acid freezes, and when heated to 86° C. it boils and is partially decomposed. Commercial nitric acid is sometimes sold under the name of *aqua fortis,* meaning *strong water.* The ordinary chemically pure acid of commerce has a specific gravity of 1.42 and contains 70 per cent. of HNO_3.

41. Uses of Nitric Acid.—From a commercial standpoint, nitric acid, after sulphuric acid, is probably the most important. It is employed for etching metals, for oxidizing various substances, for forming certain substitution products, such as nitrobenzol and picric acid, and for the preparation of

explosives such as guncotton, nitroglycerine, etc. As all the metals in common use, except gold, platinum, and aluminum, are attacked by it, this acid is employed to distinguish and separate the first two metals from others of less value. A method of finding out whether jewelry is made of gold is to touch it with a glass stopper moistened with nitric acid. This acid does not affect gold but under its influence the base alloys turn blue, on account of the formation of copper nitrate. The touchstone allows this method of testing to be applied with great accuracy. It consists of a species of black basalt obtained chiefly from Silesia. If a piece of gold is drawn across its surface, a golden streak is left, which is not affected by moistening with nitric acid; while the streak left by brass, or any similar base alloy, is readily dissolved by the acid. Experience enables an operator to determine by means of the touchstone pretty nearly the amount of gold in an alloy, comparison being made with the streaks left by gold alloys of known composition.

42. Commercial Uses for Nitric Acid.—Nitric acid reacts with many organic compounds, such as phenol or carbolic acid, toluene, glycerine, and cellulose, or ordinary cotton or wood fibers, to form nitro-compounds. Thus, when nitric acid is heated with phenol or carbolic acid, C_6H_5OH, picric acid, or trinitrophenol, is formed, $C_6H_2(NO_2)_3OH$.

$$C_6H_5OH+3HNO_3=C_6H_2(NO_2)_3(OH)+3H_2O$$

When nitric acid is heated with toluene, $C_6H_5CH_3$, trinitrotoluene, or *TNT*, is formed:

$$C_6H_5CH_3+3HNO_3=CH_3C_6H_2(NO_2)_3+3H_2O$$

These substances are used as explosives. Trinitrotoluene may be said to be one of the safest and most powerful of all modern high explosives. The actual manufacture of these substances is not so simple as it appears from the above reactions, and it is attended by more or less danger, depending on the purity of the reacting substances, temperature control, etc. Three molecules of water are formed in each reaction and in order to remove this water as soon as formed, and so facilitate the reaction as far as speed and yield of product are concerned, sulphuric acid, mixed with the nitric acid, is used. Technically,

a mixture of nitric and sulphuric acids is known as *mixed acid.* Standard mixed acid consists of 36 per cent. nitric, 61 per cent. sulphuric acid, and 3 per cent. water.

43. Glycerine, $C_3H_5(OH)_3$, which is a tri-hydric alcohol, reacts with nitric acid in a somewhat different manner. In this case, although the product formed is called nitroglycerine, it is really a nitrate of glycerine, the NO_3 group being present as in any nitrate, while in a nitro-compound the NO_2 or nitro group is present:

$$C_3H_5(OH)_3+3HNO_3=C_3H_5(NO_3)_3+3H_2O$$

Guncotton is made by the action of mixed acid on ordinary cotton or cellulose and the reaction may be represented as follows:

$$\underset{\text{(cellulose)}}{(C_6H_{10}O_5)_2}+6HNO_3=C_{12}H_{14}O_4(NO_3)_6+6H_2O$$

NOTE.—The reactions described should not be carried out by inexperienced persons, because of the danger involved. Organic compounds, such as phenol, toluene, cellulose, and glycerine, are more fully described under Organic Chemistry.

NITROUS OXIDE

Formula N_2O. Molecular weight 44.016

44. Preparation.—Nitrous oxide may be prepared by carefully heating ammonium nitrate, NH_4NO_3, to about 240° C.

$$NH_4NO_3+\text{heat}=N_2O+2H_2O$$

Above 240° C., the reaction proceeds very rapidly and there is danger of the nitrate exploding. For this reason, it is probably better to prepare the gas by heating a mixture of ammonium sulphate and sodium nitrate,

$$(NH_4)_2SO_4+2NaNO_3+\text{heat}=2N_2O+Na_2SO_4+4H_2O$$

The reaction in this case proceeds quietly.

45. Properties.—Nitrous oxide is a colorless gas with a faint, sweetish odor and a distinctly sweet taste. It may be condensed to a liquid by a pressure of 32 atmospheres at 0° C., or at ordinary pressure at −88° C. The liquid freezes also by

its own evaporation, when allowed to escape into the open air, producing a snowlike mass. Solid nitrous oxide melts at −102.3° C., and the liquid boils at −89.8° C. The gas is quite soluble in cold water, 130.5 parts of it dissolving in 100 parts of water at 0° C., and only 60.8 parts in 100 parts of water at 24° C. It is still more soluble in alcohol and in alkaline solutions.

46. Nitrous oxide supports combustion almost as vigorously as oxygen; a wax taper having a spark on its wick is relighted in it, as in oxygen. Phosphorus, as well as sulphur, burns in it with great brilliance, the gas being decomposed and its oxygen uniting with the combustible, forming oxides, while the nitrogen is liberated.

$$P_4+10N_2O=2P_2O_5+10N_2$$
$$S+3N_2O=SO_3+3N_2$$

Nitrous oxide acts as an anesthetic when inhaled (that is, it is a substance that causes insensibility to pain). The anesthetic effects of this gas were discovered by Wells, and acknowledged as the crowning surgical discovery of the 19th century. About 4 or 5 gallons of the gas is sufficient in most cases to produce total insensibility. Before this stage is reached, it induces a state of intoxication, often accompanied by violent fits of laughter, and for this reason it is called laughing gas.

NITRIC OXIDE

Formula NO. Molecular weight 30.008

47. History and Preparation.—Nitric oxide, though really discovered by Mayow (1669) was first investigated thoroughly by Priestley in 1772. It may be obtained by the action of nitric acid on copper, without the application of heat. The nitric acid first oxidizes the copper, as shown by the equation:

$$\underset{\text{copper}}{3Cu} + \underset{\substack{\text{nitric}\\\text{acid}}}{2HNO_3} = \underset{\substack{\text{copper}\\\text{oxide}}}{3CuO} + \underset{\text{water}}{H_2O} + \underset{\substack{\text{nitric}\\\text{oxide}}}{2NO}$$

The copper oxide formed is at once dissolved by the excess of nitric acid, according to the equation:

$$\underset{\text{copper oxide}}{3CuO}+\underset{\text{nitric acid}}{6HNO_3}=\underset{\text{copper nitrate}}{3Cu(NO_3)_2}+\underset{\text{water}}{3H_2O}$$

Or the two reactions may be stated in one equation, thus:

$$\underset{\text{copper}}{3Cu} + \underset{\text{nitric acid}}{8HNO_3}=\underset{\text{copper nitrate}}{3Cu(NO_3)_2} + \underset{\text{nitric oxide}}{2NO} + \underset{\text{water}}{4H_2O}$$

Nitric oxide may also be prepared by heating ferrous sulphate with a mixture of nitric and sulphuric acids:

$$6FeSO_4+3H_2SO_4+2HNO_3=3Fe_2(SO_4)_3+2NO+4H_2O$$

or by the action of nitric acid on mercury:

$$3Hg+8HNO_3=3Hg(NO_3)_2+2NO+4H_2O$$

A purer product may be obtained, however, by reducing potassium nitrate with ferrous chloride and hydrochloric acid:

$$KNO_3+3FeCl_2+4HCl=3FeCl_3+KCl+2H_2O+NO$$

48. Properties.—Nitric oxide is a colorless gas which in contact with the air combines with the oxygen to form nitrogen peroxide, a gas of a reddish-brown color. Because of its affinity for oxygen, it is impossible either to taste or smell the gas. The strong odor arising during its preparation is due to the higher oxides of nitrogen and not to nitric oxide.

Nitric oxide is slightly heavier than air, having a specific gravity of 1.0367. It is more difficult to liquefy than nitrous oxide, its critical temperature being −93.5° C. and its critical pressure, 71.2 atmospheres. The gas is insoluble in boiling water and only 7.3 parts dissolve in 100 parts of water at 0° C. Liquid nitric oxide freezes to a solid, which melts at −167° C., and the liquid boils at −150.2° C. It is much more stable than nitrous oxide, and may be subjected to even a red heat without undergoing decomposition. In consequence of this property, it does not accelerate combustion, as a lighted taper plunged into a jar filled with it is immediately extinguished.

NITROGEN PEROXIDE

Formulas NO_2 or N_2O_4. Molecular weights 46.008 or 92.016

49. Preparation.—Nitrogen peroxide may be prepared by mixing 2 volumes of nitric oxide with 1 volume of oxygen, when they combine according to the equation:

$$2NO+O_2=2NO_2$$

It is generally prepared by heating perfectly dry lead nitrate, which decomposes thus:

$$2Pb(NO_3)_2=2PbO+O_2+4NO_2$$

50. Properties.—Upon cooling the gases evolved, by means of a freezing mixture, the peroxide is condensed to a liquid, and the oxygen escapes. If perfectly dry, the peroxide congeals to a white crystalline solid at about $-9.6°$ C. At 0° C. the liquid has a faint yellow color that gradually grows darker as the temperature is increased until it is a deep orange at about 21.6° C., at which point the liquid boils, giving off an orange vapor.

At very low temperatures the formula of the peroxide is N_2O_4, but this dissociates in proportion to the temperature until 150° C. is reached, when the formula is NO_2. N_2O_4 is colorless and NO_2 is colored, so the yellow color at 0° C. shows that dissociation has already commenced, and between this and 150° C. the peroxide is a mixture of N_2O_4 and NO_2. Above this the formula is NO_2. Water decomposes the peroxide, the products depending on the temperature. If the water is cold, nitrous and nitric acids are formed, thus:

$$2NO_2+H_2O=HNO_2+HNO_3$$

If the water is hot, nitric acid and nitric oxide are formed, thus:

$$3NO_2+H_2O=2HNO_3+NO$$

The NO formed unites with oxygen of the air, forming NO_2, and this acts on a further quantity of hot water, as above, until all the oxide is converted into nitric acid. Nitrogen peroxide is an energetic oxidizing agent.

NITROGEN TRIOXIDE AND NITROUS ACID

Formulas N_2O_3 and HNO_2. Molecular weight of the oxide 76.016; of the acid, 47.016.

51. Preparation.—Nitrogen trioxide may be prepared by the reduction of nitric acid by arsenious oxide:

$$2HNO_3+As_2O_3=2HAsO_3+N_2O_3$$

52. Properties.—Upon cooling the vapors evolved, by means of a freezing mixture, the nitrogen trioxide condenses to a rather unstable greenish-blue liquid that reacts with water and produces nitrous acid.

Nitrous acid is a blue liquid, rather unstable at ordinary temperatures, but it may be preserved unaltered at a low temperature. At ordinary temperatures it is readily decomposed into nitric acid, water, and nitric oxide, thus:

$$3HNO_2=HNO_3+H_2O+2NO$$

The salts of nitrous acid are known as nitrites, and are stable.

Nitrogen trioxide is sometimes called nitrous anhydride, since, on coming in contact with water, nitrous acid is produced:

$$N_2O_3+H_2O=2HNO_2$$

Nitrous acid is best prepared, however, by the action of hydrochloric acid on a nitrite. Thus, sodium nitrite may be first prepared by heating a mixture of sodium nitrate with metallic lead:

$$NaNO_3+Pb=PbO+NaNO_2$$

and by treating sodium nitrite in water solution with a little hydrochloric acid, a solution of nitrous acid is obtained:

$$NaNO_2+HCl=NaCl+HNO_2$$

NITROGEN PENTOXIDE

Formula N_2O_5. Molecular weight 108.016

53. Preparation.—Nitrogen pentoxide, the constitution of which was first established by Deville in 1849, may be prepared by treating nitric acid with phosphorus pentoxide, a sub-

stance that has a strong affinity for water, when the following reaction takes place:

$$2HNO_3+P_2O_5=N_2O_5+2HPO_3$$

It is more readily obtained by passing chlorine over silver nitrate and condensing the product. The reaction is:

$$4AgNO_3+2Cl_2=4AgCl+O_2+2N_2O_5$$

Nitrogen pentoxide is a colorless, transparent solid that crystallizes in right rhombic prisms. It melts at 30° C. and boils at 47° C. It is very unstable, sometimes exploding spontaneously. It reacts energetically with water, producing nitric acid according to the equation:

$$N_2O_5+H_2O=2HNO_3$$

and it is therefore sometimes called nitric anhydride.

HYPONITROUS ACID

Formula $H_2N_2O_2$. Molecular weight 62.032

54. Preparation.—Hyponitrous acid may be prepared by reducing a nitrate. Thus, when a solution of potassium nitrate is treated with sodium amalgam (a solution of metallic sodium in mercury) the nascent hydrogen liberated by the action of the sodium on the water of the solution reduces the potassium nitrate and forms potassium hyponitrite:

$$2KNO_3+8H=K_2N_2O_2+4H_2O$$

Sodium hydroxide is also formed and if the alkaline solution is neutralized with acetic acid (treated in the Sections dealing with the subject of organic chemistry) and silver nitrate is added, a yellow precipitate of silver hyponitrite, $Ag_2N_2O_2$, is formed:

$$K_2N_2O_2+2AgNO_3=Ag_2N_2O_2+2KNO_3$$

If this is filtered off and treated with a solution of hydrochloric acid gas in dry ether, hyponitrous acid is set free:

$$Ag_2N_2O_2+2HCl=H_2N_2O_2+2AgCl$$

The insoluble silver chloride formed is then filtered off and upon evaporating the ethereal filtrate, white, deliquescent plates of hyponitrous acid are obtained.

Hyponitrous acid is also formed by the action of nitrous acid on hydroxylamine:

$$HNO_2+NH_2OH=H_2N_2O_2+H_2O$$

When freed from water, hyponitrous acid is very explosive. In water solution it is also very unstable, decomposing into water and nitrous oxide:

$$H_2N_2O_2=H_2O+N_2O$$

55. Balancing of Equations.—In discussing the action of nitric acid on the metals, certain equations were given which cannot be readily balanced unless the changing valences of the elements concerned are taken into consideration. Several equations were also given which are not readily balanced by any one method, the correct result being obtained only by a combination of methods. The following examples will illustrate the application of the methods used:

1. Consider the reaction which takes place between copper and dilute nitric acid. The skeleton equation is written:

$$Cu+HNO_3=Cu(NO_3)_2+NO+H_2O$$

In HNO_3 nitrogen has a valence of 5 while in NO its valence is reduced to 2. This reduction is due to copper. Therefore, the coefficient 3 is placed before Cu on the left and $3Cu(NO_3)_2$ on the right:

$$3Cu+HNO_3=3Cu(NO_3)_2+NO+H_2O$$

There are now 6 (NO_3) radicals in $3Cu(NO_3)_2$, so the coefficient 6 is placed before HNO_3:

$$3Cu+6HNO_3=3Cu(NO_3)_2+NO+H_2O$$

Copper on the left has a zero valence, while on the right it has a valence of 2. This increase is due to HNO_3 and 2 is added to the coefficient already present.

$$3Cu+8HNO_3=3Cu(NO_3)_2+NO+H_2O$$

There are now 8 nitrogens on the left and only 7 on the right; the coefficient 2 is, therefore, placed before NO:

$$3Cu+8HNO_3=3Cu(NO_3)_2+2NO+H_2O$$

At this stage there are 8 hydrogen atoms and 24 oxygen atoms on the left and 2 hydrogen atoms and 21 oxygen atoms

on the right and in order to make both the hydrogen and oxygen atoms balance the coefficient 4 is placed before H_2O:

$$3Cu+8HNO_3=3Cu(NO_3)_2+2NO+4H_2O$$

2. Consider the reaction, the skeleton equation for which may be written,

$$FeSO_4+H_2SO_4+HNO_3=Fe_2(SO_4)_3+NO+H_2O$$

As in the preceding case, the difference between the valence of nitrogen in HNO_3 and NO is 3. This decrease is due to ferrous sulphate, so the coefficient 3 is placed before $FeSO_4$:

$$3FeSO_4+H_2SO_4+HNO_3=Fe_2(SO_4)_3+NO+H_2O$$

Now there are 3 Fe atoms on the left and 2 on the right and to make each side balance, it is necessary merely to multiply $3FeSO_4$ by 2 and $Fe_2(SO_4)_3$ by 3:

$$6FeSO_4+H_2SO_4+HNO_3=3Fe_2(SO_4)_3+NO+H_2O$$

On inspection it is seen that there are 9 (SO_4) radicals on the right and only 7 on the left. Therefore, the coefficient 3 is placed before H_2SO_4:

$$6FeSO_4+3H_2SO_4+HNO_3=3Fe_2(SO_4)_3+NO+H_2O$$

The hydrogen atoms are not yet balanced, since there are 7 on the left and only 2 on the right. This is another case of an uneven coefficient, and since it is impossible to place an even coefficient before H_2O and thereby cause the hydrogen atoms to balance, the hydrogen on the left is increased to 8 atoms by writing $2HNO_3$ and 4 placed before H_2O:

$$6FeSO_4+3H_2SO_4+2HNO_3=3Fe_2(SO_4)_3+NO+4H_2O$$

All of the atoms with the exception of nitrogen and oxygen now balance and this can be accomplished by placing the coefficient 2 before NO:

$$6FeSO_4+3H_2SO_4+2HNO_3=3Fe_2(SO_4)_3+2NO+4H_2O$$

CARBON

Symbol C. Atomic weight 12.005

56. Occurrence.—Carbon is the most important constituent of all organic substances. It occurs in the free state in nature in two crystalline forms known as diamonds and graphite. When an organic compound is heated with a limited amount of air, a portion of the carbon remains as amorphous* carbon. Carbon also occurs in peat and lignite and in bituminous and anthracite coal. In combination with hydrogen, it occurs in mineral oils. It also occurs in the air as carbon dioxide, and in minerals and rocks in the form of a carbonate.

57. Preparation.—By heating wood or coal in a closed vessel, carbon in an impure state may be readily obtained. Water and volatile compounds of carbon with hydrogen and oxygen are driven off; the excess of carbon remains, together with the non-combustible portions of the wood or other substance.

This process of heating a body and causing its decomposition, in part, into gaseous and liquid products, which are collected, is termed destructive distillation.

58. The Diamond.—The form of carbon known as a diamond is, when cut, a brilliant, transparent, and usually colorless solid; it has a specific gravity of 3.5 and is found in different crystalline forms. It is the hardest substance known, and can only be scratched or polished by rubbing it with diamond powder or dust. The colorless stones and those which are delicately tinted are the most valuable. The black diamond, or carbonado, is used for grinding purposes and glass cutting. The so-called diamond drill consists of a steel tube around the edge of which black diamonds are mounted. When this drill is used a cylindrical specimen or core of the rock strata through which it passes is obtained for examination. The diamond is a non-conductor of electricity.

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*Amorphous means non-crystalline or without crystalline structure. Paraffin and beeswax are also common examples of amorphous substances.

59. Artificial diamonds were first made by Moissan in 1887 who dissolved carbon in molten iron, which was subsequently chilled, causing an enormous pressure to be exerted upon the dissolved carbon. After thoroughly cooling, the mass was broken up and treated with acid to dissolve the iron, the insoluble residue being found to contain a few microscopic fragments, which were recognized as diamonds.

60. Graphite.—Graphite is found in large quantities in Siberia, India, Ceylon, and in the state of California.

Molten iron, containing silicon, *Si*, is capable of dissolving large quantities of carbon, which, upon the cooling of the iron, is deposited as graphite.

Graphite is now manufactured by heating a mixture of amorphous carbon, coke, charcoal, or anthracite, and a little sand in an electric furnace. Carbon alone, in one of its various forms, such as coke, charcoal, etc., cannot be converted into graphite, the change taking place through the intermediate formation of a carbide.

Graphite is a soft, shiny, grayish-black substance, which is smooth to the touch. It is usually found in compact laminated masses, but sometimes crystallized in six-sided plates. It has a specific gravity of 2.5 and is a good conductor of heat and electricity.

Graphite is used in the manufacture of lead pencils and plumbago crucibles; it is also used for glazing and for black polishing powder. Graphite may serve as a lubricant where oil cannot be used, on account of high temperatures, and also as a protective coating for ironwork.

61. Amorphous Carbon.—The modification of carbon known as amorphous carbon is formed by the carbonization of organic compounds. The amorphous carbon produced in this manner is named to indicate its origin or method of production. The principal forms are: (*a*) Coal; (*b*) lampblack; (*c*) wood charcoal; (*d*) animal charcoal; (*e*) gas carbon; and (*f*) coke.

(*a*) *Coal.*—The purest variety of coal is known as anthracite, which is an amorphous, black, hard, and somewhat lus-

trous body; it is rather hard to ignite, and has lost all its organic structure. From this variety there is a regular graduation through cannel and bituminous coals of all varieties to lignite, or brown coal, which is sometimes only slightly altered wood. All coal is derived from primitive vegetation, which has been changed and consolidated by heat and pressure. Anthracite is found where the strata have been most exposed to heat or disturbed by volcanic motions; bituminous is found where the strata are nearly or quite horizontal, while brown coal is much more recent in age and retains the characteristics of its vegetable origin.

Table III gives the percentages of fixed carbon and volatile matter in the various kinds of coals.

(*b*) *Lampblack.*—Lampblack is the soot or amorphous carbon obtained by burning bodies rich in carbon with an insufficient supply of air. Resin or petroleum are burned with less air than is required for perfect combustion, the smoky products of this combustion passing into chambers hung with coarse cloths, on which the lampblack is deposited. The finest grades of lampblack are prepared by depositing the soot on metal cylinders revolving over the burners. Lampblack is purified by heating it in closed vessels.

TABLE III

CARBON CONTENT OF COALS

Coal	Fixed Carbon Per Cent.	Volatile Matter Per Cent.
Anthracite	97.0 to 92.5	3.0 to 7.5
Semianthracite	92.5 to 87.5	7.5 to 12.5
Semibituminous	87.5 to 75.0	12.5 to 25.0
Eastern bituminous	75.0 to 60.0	25.0 to 40.0
Western bituminous	65.0 to 50.0	35.0 to 50.0
Lignite	under 50	over 50

Diamond black is an extremely pure quality of lampblack made by the imperfect combustion of natural gas, particularly

from that of the Ohio petroleum regions. Lampblack is used as a pigment for both oil and water colors as well as for liquid and drawing ink. It forms the chief ingredient in India ink and printing ink, and in the preparation of some kinds of leather.

(*c*) *Wood Charcoal.*—Wood charcoal is a form of carbon prepared from wood burned with little access of air. Bil-

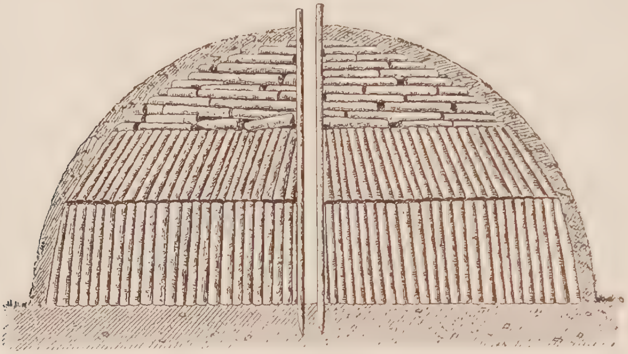


Fig. 3

lets of wood are built up into a heap, Fig. 3, around stakes driven into the ground and the heap is then covered with earth or sand. The heap is fired at openings left at the bottom of the pile. For making fine charcoal, such as that of willow charcoal, the wood is burned in iron cylinders or retorts. In this method, which is a process of destructive distillation, the volatile products, such as wood spirits, pyroligneous acid, and tar, are collected.

Good charcoal has a pure black color, and a glittering fracture. It is used as a fuel, a polishing powder, an absorbent of gases and aqueous vapor; also as a non-conductor of heat, as an ingredient in fireworks and in gunpowder.

(*d*) *Animal Charcoal.*—Animal charcoal, or bone black, is obtained by calcining bones in closed vessels. These vessels are either retorts similar to those in which coal is distilled for the production of illuminating gas or they are earthenware pots piled up in kilns, and fired. After being burned, the bones are ground in fluted rolls, and the dust removed.

Animal charcoal is a black, porous mass, used in sugar refining and in other manufacturing processes as a decolorizing and filtering agent.

(*e*) *Gas Carbon.*—Gas carbon, next to lampblack, is the purest form of amorphous carbon. It is formed, as its name implies, in the manufacture of coal gas and appears as an iron-gray deposit in the upper part of the retorts. Gas carbon is a good conductor of heat and electricity and is used for batteries and as carbons for electric arc lamps.

(*f*) *Coke.*—Coke is one of the products of the distillation of coal in ovens and retorts. It bears the same relation to coal as charcoal does to wood. Coke was originally produced by burning coal in heaps with a limited supply of air. This occasioned a considerable loss of coal and led to the building of coke ovens, the coke produced in this way being found to be much harder, denser, and less combustible than that made in open heaps.

The most efficient method of coking is by means of coke ovens, of which there are many kinds, but the principle of operation and the object in view are the same in all. The simplest oven is the beehive oven, which is built of brick and is charged from the top from coal cars running on rails on the top of a series of ovens. The volatile matter escapes through the charging openings and the coke is removed through a door in the front of the oven. After the coal has been heated for about 36 hours the coke is raked out and quenched with water. The heat required to carry on the combustion is obtained by the burning of part of the coal and in some plants by the volatile, combustible gases which are given off.

By-product coking ovens are now coming to be used extensively in this country. They are much more economical than beehive ovens, as they utilize practically all of the gases given off, besides saving the products of distillation of the coal.

62. Properties of Carbon.—The great difference in the properties exhibited by the diamond, graphite, and charcoal naturally leads to the belief that they consist of dissimilar carbon molecules. Very recent researches have shown that the

difference in the character and properties of these three varieties of carbon is due to a difference in the internal energy of each, the diamond having the most internal energy and charcoal having the least.

63. Although carbon shows a remarkable indisposition to unite directly with other elements, the compounds it forms with hydrogen are very numerous. They are therefore treated in the Sections on organic chemistry. It was at first thought that these compounds could be formed only as the result of natural phenomena, but it is now known that they can be prepared in the laboratory, and that they are subject to the same laws as inorganic compounds. Only the more common compounds of carbon and hydrogen will be discussed in the Sections treating on the subject of inorganic chemistry.

64. Uses of Carbon.—The various kinds of carbon are employed for different purposes. Lampblack is used largely in the preparation of inks and paints; gas carbon, or coke, is used in the electrical industries for electrodes, parts of batteries, etc.; wood charcoal is used in the manufacture of black powder; animal charcoal, or bone black, is often employed for filtering purposes, as it removes coloring matter, objectionable gases, and lead salts from drinking water. Large quantities are also used in the sugar industry to decolorize sugar solutions. During the recent war, both wood and animal charcoals were used to a great extent as catalyzers in the manufacture of phosgene gas, and as absorbents for poisonous gases in the manufacture of gas masks in which charcoal made from fruit pits and coconut shells gave the best results.

CARBON AND OXYGEN

65. There are two well known oxides of carbon, namely, carbon monoxide, CO, and carbon dioxide, CO_2. The former is the product of the incomplete oxidation of carbon, the latter the final product of the oxidation of carbon. Carbon dioxide is the more important and will therefore be studied first.

CARBON DIOXIDE

Formula CO_2. *Molecular weight 44.005*

66. History.—It has been stated that carbon dioxide —sometimes called carbonic-acid gas—is a component of the air. It was the first gas distinguished from it, being noticed as a distinct substance by Paracelsus in 1520, while soon after Van Helmont obtained it from limestone—for which reason he called it chalky air—and noticed also its production in the fermentation of sugar and in the burning of charcoal. Black showed in 1757 that alkalies absorbed it and that its compounds effervesced with acids. Lavoisier in 1775 determined its composition synthetically by burning carbon in oxygen.

67. Occurrence.—Carbon dioxide occurs widely distributed in nature. It occurs free in the air, in which it is always present, but of which it forms a small part—about .04 per cent. It is always present also in the soil, due to the decomposition of organic matter. It is found in many mineral springs and in the earth in great abundance in the form of carbonates, as limestone, marble, magnesite, dolomite, etc.

68. Preparation.—Carbon dioxide can be produced in a number of ways, of which only the following three methods will be considered:

1. By combustion of carbon with an excess of oxygen:

$$C+O_2=CO_2$$

2. When limestone is heated, it is decomposed, the products of the decomposition being quicklime and carbon dioxide.

$$CaCO_3+\text{heat (825° C.)}=CaO+CO_2$$

3. When limestone or marble, which consist largely of calcium carbonate, are treated with dilute hydrochloric acid, HCl, the products formed are calcium chloride, $CaCl_2$, carbon dioxide, and water.

$$CaCO_3+2HCl=CaCl_2+H_2O+CO_2$$

In this method, which is generally used in the laboratory, the gas is purified by passing it through a solution of sodium

bicarbonate and then drying by passing it through a tube containing fused, or anhydrous, calcium chloride.

69. Chemical Properties.—Carbon dioxide is a very stable compound, being only slightly decomposed at temperatures as high as 2,000° C. It unites directly with the oxides of the alkalies such as sodium and potassium oxides, to form the carbonates. Carbon dioxide is non-combustible and does not support combustion. Although the gas is poisonous when inhaled in sufficient quantity, it does not possess toxic properties, but causes death by suffocation or by the exclusion of oxygen from the lungs. If a quantity of about 5 per cent. of the gas is present in air it will extinguish a lighted taper, but air containing this amount of the gas will support respiration for a short time.

70. Physical Properties.—Carbon dioxide is a colorless gas having a slightly pungent odor and an acid taste, best described as being that of a freshly opened bottle of soda water. It is about one and a half times heavier than air, its specific gravity being 1.53. At 0° C., 179.67 parts of the gas dissolve in 100 parts of water and at 20° C., 90.14 parts dissolve in 100 parts of water. Carbon-dioxide gas may be liquefied at a temperature of 31° C. under a pressure of 72.85 atmospheres. The liquid boils at −72.8° C., and may be frozen to a solid, melting at −65° C.

71. Uses of Carbon Dioxide.—Gaseous carbon dioxide is used in large quantities in the manufacture of sodium bicarbonate, or baking soda, $NaHCO_3$, and of the normal salt, $Na_2CO_3 \cdot 10H_2O$, or washing soda, and in the manufacture of white lead, which is a basic carbonate, $Pb_3(OH)_2(CO_3)_2$.

As mentioned above, the gas does not burn, and since a small percentage of it destroys the power of air to support combustion, it is used in fire extinguishers that depend upon the action of sulphuric acid on a solution of sodium bicarbonate, carbon dioxide being liberated; thus:

$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2H_2O + 2CO_2$$

CARBONIC ACID

Formula H_2CO_3. *Molecular weight 62.021*

72. Preparation.—Carbonic acid is produced when carbon dioxide is dissolved in water,

$$CO_2+H_2O=H_2CO_3$$

It is, however, unstable, and has not been obtained free from water because it decomposes too readily into water and carbon dioxide on slightly raising the temperature or by freezing it. The solution in water is distinctly though feebly acid. It possesses the pungent odor and agreeable acid taste well known in so-called soda water. The existence of this acid is proved by the fact that the aqueous solution will redden blue litmus paper although the dry carbon dioxide has no effect.

73. Salts of Carbonic Acid.—Although carbonic acid itself is very unstable, its salts, the carbonates, are very stable compounds. Being a dibasic acid, normal and acid salts are formed. When carbon dioxide is passed into solutions of the *alkali hydroxides,* the normal carbonates, which are soluble in water, are formed according to the equation:

$$2NaOH+CO_2=Na_2CO_3+H_2O$$

If these carbonates are again treated with carbon dioxide, the acid salt, or bicarbonate, is formed; thus:

$$Na_2CO_3+H_2O+CO_2=2NaHCO_3$$

The normal carbonates of the alkaline earths—barium, calcium, and strontium—can be prepared in the same way, but they are insoluble in water. The alkaline-earth carbonates dissolve in an excess of carbonic acid, forming the bicarbonates, which are soluble in water.

$$BaCO_3+2H_2CO_3=Ba(HCO_3)_2+CO_2+H_2O$$

74. Carbonates may be either normal, acid, or basic. A *normal carbonate* is one in which all the hydrogen of carbonic acid has been replaced by a metal or group of elements, as sodium carbonate, Na_2CO_3, barium carbonate, $BaCO_3$, or ammonium carbonate, $(NH_4)_2CO_3$. An *acid carbonate* is one

in which only one-half of the hydrogen has been replaced by a metal, as in acid sodium carbonate, or sodium bicarbonate, $NaHCO_3$. A *basic carbonate* is a normal carbonate in combination with an oxide or hydroxide of the metal, as in white lead, basic lead carbonate, $Pb_3(OH)_2(CO_3)_2$, which is formed as the result of the reaction between solutions of lead nitrate and sodium carbonate:

$$3Pb(NO_3)_2+3Na_2CO_3+H_2O=Pb_3(OH)_2(CO_3)_2 \\ +6NaNO_3+CO_2$$

Strange as it may appear, all the normal carbonates of the alkalies give an alkaline reaction and the bicarbonates or acid carbonates of the alkalies are neutral to phenolphthalein.

75. Hard and Soft Waters.—The student will have noticed from daily experience that certain kinds of water when mixed with a very small quantity of soap immediately produce a lather, and that the water imparts that peculiar quality to the hands which is generally known as soapiness; such water is termed soft water. Other waters when used with soap for washing purposes do not lather at all readily and do not cause soapiness until a considerable quantity of soap has been consumed. When lather is actually formed, there will be found on examination a layer of scum on the surface of the water. Such water is termed hard water.

Without going into the details of the composition of soap and its reaction with water when used for washing, it may be explained that soluble salts of calcium and magnesium decompose soap, forming a precipitate that constitutes the scum found when washing with hard water. Consequently, if water containing calcium salts in solution is employed for washing purposes, sufficient soap must first be added to precipitate these salts before any is available for cleansing; hence, hard waters are neither so agreeable nor so economical for washing purposes.

The principal calcium and magnesium salts found in water are the carbonate and the sulphate. The carbonates may be precipitated by the act of boiling and any hardness due to their presence may be thus remedied. Consequently, any

hardness produced by carbonates of calcium or magnesium is termed temporary hardness.

The sulphates and chlorides of calcium and magnesium are not precipitated by boiling, as their solution is caused by the water itself and not by water in addition to carbon-dioxide gas. Therefore, hardness due to the presence of sulphates or chlorides of calcium or magnesium is called permanent hardness.

The hardness of most waters is partly temporary and partly permanent, the two together constituting what is known as the total hardness of the water.

76. The hardness of the water is usually tested by taking a measured quantity of the water and adding thereto in a stoppered bottle a solution of soap in alcohol of a known strength. This is introduced in small quantities at a time from a measuring instrument such as a burette, the water being well shaken after each addition. As soon as a lather that stands unbroken for about 5 minutes is produced, the quantity of soap solution used is read off; from this the total hardness is determined. A sample of the water is next boiled until the carbonates are precipitated; then, after certain precautions the hardness is again determined with the soap solution. This gives the temporary hardness, which is the difference between total and permanent hardness.

77. Processes of Softening Water.—Water may be softened and the temporary hardness removed by boiling for some minutes. Potassium, and sodium carbonates precipitate calcium and magnesium salts, and possess detergent, or washing, properties; therefore, these salts will remove hardness, whether temporary or permanent. One of the characteristics of potassium and sodium carbonates is their power to impart a soapy feeling to pure water. Ordinary washing soda, or soda crystal, is commercial sodium carbonate.

A most interesting process for softening water is the one named Clark's process. It is based on the facts that calcium bicarbonate is soluble in water while the normal carbonate is insoluble, and that the hydrogen of the soluble bicarbonate

may be replaced by calcium, forming the insoluble normal carbonate. To soften water by Clark's process, lime water is added in just sufficient quantity to replace all the hydrogen of the bicarbonate. The whole of the calcium originally present in the water as carbonate and that added as hydroxide, is precipitated, and the temporary hardness is thus removed. The chemical reaction is represented in the following equation:

$CaH_2(CO_3)_2$	$+$	$Ca(OH)_2$	$=$	$2CaCO_3$	$+$	$2H_2O$
soluble calcium bicarbonate		lime water (calcium hydroxide)		insoluble calcium carbonate formed from the bicarbonate and hydroxide		water

The precipitated calcium carbonate is removed either by allowing it to subside or by filtration.

CARBON MONOXIDE

Formula CO. Molecular weight 28.005

78. History and Occurrence.—Carbon monoxide, an extremely **poisonous** gas, was discovered by Lassone in 1776, and independently by Priestley in 1783; its true nature and exact composition were determined by Woodhouse in 1800. Every one is familiar with the appearance of a coke or charcoal fire or of a coal fire that has burned perfectly clear and smokeless —the whole mass glows with a bright red heat and hovering over the top are lambent blue flames. The origin of these characteristics may be explained in this way: In the lower parts of the grate where air enters the fire, carbon dioxide is formed according to the equation

$$C+O_2=CO_2$$

This carbon dioxide passes upwards through the red-hot carbon and is reduced to carbon monoxide, with the result that an inflammable gas is produced:

$$CO_2+C=2CO$$

In general it may be stated that when carbon is burned without a sufficient supply of air, carbon monoxide is formed as one of the products of combustion.

79. Preparation.—In the laboratory, carbon monoxide is most conveniently prepared by heating certain organic compounds with sulphuric acid. This acid acts merely as a dehydrating agent, that is, it absorbs the water formed by the reaction, and it may be subsequently recovered although in a very dilute state.

Oxalic acid when treated with sulphuric acid in the above manner splits up into water, carbon dioxide, and carbon monoxide, thus:

$$\underset{\text{oxalic acid}}{H_2C_2O_4} = \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2} + \underset{\text{carbon monoxide}}{CO}$$

and when this method is used, the gas must be passed through a solution of sodium or potassium hydroxide to remove the carbon dioxide. Fig. 4 shows the general arrangement of the apparatus.

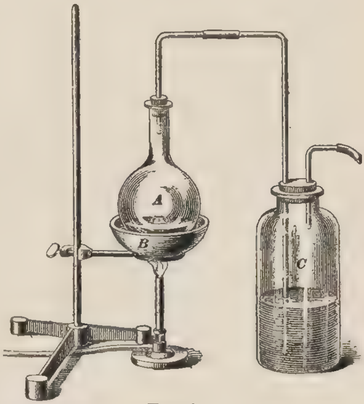


FIG. 4

The flask *A*, which contains the oxalic acid and the sulphuric acid, rests in a sand bath *B*, the evolved gas being sent through a tube into the wash bottle *C* containing a solution of sodium hydroxide. The gas passes from *C* out through the delivery tube and is either *immediately* lighted or it is passed into a suitable collector for storage. Under no circumstances should the gas be allowed to escape into the laboratory.

80. Formic acid, $HCHO_2$, on being similarly heated with concentrated sulphuric acid, yields pure carbon monoxide, according to the following equation:

$$HCHO_2 = H_2O + CO$$

and in this case the wash bottle *C* may be dispensed with.

81. Chemical Properties.—Carbon monoxide is a combustible gas burning readily in the air or in oxygen with a

characteristic lambent blue flame. Though inflammable, it is not a supporter of combustion. When burned, its own volume of carbon dioxide is produced, half of its own volume of oxygen being required:

$$2CO+O_2=2CO_2$$

Mixed with moist air or moist oxygen, it forms an explosive mixture. When perfectly dry, however, no explosion occurs and the combination takes place slowly.

It is totally unfit for breathing, being an active poison, 1 per cent. of carbon monoxide in the air proving fatal when breathed.

82. Carbon monoxide belongs to that class of compounds described in the Sections treating of the subject of organic chemistry as being unsaturated. In this compound, C has a valence of 2 and the formula may be written $C=O$, showing C and O connected by means of a double bond. This kind of a linking between atoms is regarded as a weak one and the compound in which it occurs is unstable and reacts readily upon other substances to form new compounds. This explains the chemical activity of CO.

Carbon monoxide unites with chlorine in the presence of sunlight or properly prepared charcoal, which acts as a catalytic agent, to form carbonyl chloride or phosgene gas:

$$CO+Cl_2=COCl_2$$

and with sulphur to form carbon oxysulphide, COS, another gaseous substance. It also unites with nickel and iron to form the carbonyls of these metals, $Ni(CO)_4$ and $Fe(CO)_5$, both of which are liquids.

Carbon monoxide acts as a powerful reducing agent and is frequently used in metallurgical work for the production of metals from their oxides. Thus, metallic oxides like Fe_2O_3, CuO, etc. are converted into the metals at high temperatures:

$$Fe_2O_3+3CO=2Fe+3CO_2$$

An ammoniacal solution of cuprous chloride, $CuCl$, absorbs carbon monoxide. During the operation a copper compound, $Cu_2Cl_2CO{\cdot}2H_2O$, which may be isolated, is formed.

83. The so-called water gas is a mixture of carbon monoxide, carbon dioxide, and hydrogen, to which has been added hydrocarbons to increase its luminosity. It is prepared by passing steam over red-hot coke. Owing to the poisonous character of carbon monoxide, the amount permissible in a gas used for illuminating purposes is now fixed by law in most states. The average composition of water gas is generally:

Hydrogen	50 per cent.
Carbon monoxide	40 per cent.
Carbon dioxide	5 per cent.
Nitrogen (from the air and coke)	5 per cent.
	100 per cent.

84. Physical Properties.—Carbon monoxide is a colorless, tasteless gas, possesses a peculiar oppressive odor, and is extremely poisonous. It produces a painful headache even when present in the air in small quantities. It liquefies only under very great cold and pressure. The critical temperature is $-137.7°$ C., and the critical pressure, 34.6 atmospheres. Liquid carbon monoxide boils at $-192°$ C., and the liquid may be frozen to a solid, which melts at $-205.7°$ C. Gaseous carbon monoxide has a specific gravity of .967, and it is only slightly soluble in water.

COMPOUNDS OF CARBON*

METHANE

Formula CH_4. Molecular weight 16.037

85. Occurrence.—Methane occurs free in nature, being evolved during the decomposition of dead vegetable matter confined under water; hence, it is found in marshy districts and has thus received its common name of marsh gas. If stagnant water is observed closely, bubbles of the gas may be seen to

*The compounds discussed under this heading will be more fully discussed in the Sections treating on the subject of organic chemistry.

arise; these may be collected by inverting a jar, filled with water, in the pool. During the changes that have occurred while coal has been forming from vegetable growths methane has also been evolved and has remained imprisoned in the cavities of the coal. As the coal is mined, the gas escapes from these cavities into the mine and, mixing with the air, forms the explosive mixture known as firedamp. It often occurs in the vicinity of salt wells, as in Kanawha, W. Va. It is the principal constituent of the so-called natural gas that has come so extensively into use in some cities for purposes of lighting and heating.

86. Preparation.—Methane is best prepared by heating a mixture of sodium acetate and sodium hydroxide. The methane is formed according to the following equation:

$$C_2H_3O_2Na + NaOH = CH_4 + Na_2CO_3$$

It is also obtained when an electric spark is passed through a mixture of carbon monoxide and hydrogen, thus:

$$CO + 3H_2 = CH_4 + H_2O$$

Methane is obtained in a pure condition by the action of water on aluminum carbide, thus:

$$Al_4C_3 + 6H_2O = 3CH_4 + 2Al_2O_3$$

87. Properties.—Methane is a light, colorless gas, and was formerly sometimes called light carbureted hydrogen. It is odorless and tasteless, and is slightly soluble in water, but more readily soluble in alcohol. It is not a supporter of combustion, but burns with a non-luminous flame, resembling that of hydrogen, but faintly tinged with yellow. It forms an explosive mixture with oxygen or air and is the cause of the serious explosions that sometimes happen in coal mines. By the action of chlorine on methane, its hydrogen is gradually replaced by chlorine, forming successively the compounds CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. It constitutes the first member of a homologous series of hydrocarbons known as the marsh-gas series, the successive members increasing uniformly by CH_2. They are all saturated substances, having the general

formula C_nH_{2n+2}; that is, they contain twice as many atoms of hydrogen as of carbon, plus 2. They constitute the essential portion of the various native petroleums.

ETHYLENE

Formula C_2H_4. Molecular weight 28.042

88. History and Occurrence.—Ethylene, also known as ethene, olefiant gas, or heavy carbureted hydrogen, was discovered in 1796 by four Dutch chemists, Deiman, Paets von Troostwyk, Bondt, and Lauwerenburgh. It is one of the most important constituents of coal gas, being formed when the coal is subjected to destructive distillation; it has been found in small quantities among the gases of coal mines.

89. Preparation.—Ethylene is most conveniently prepared by the action of concentrated sulphuric acid on ethyl or grain alcohol, C_2H_5OH. The sulphuric acid abstracts the elements of water, hydrogen, and oxygen, from the alcohol.

$$C_2H_5OH = C_2H_4 + H_2O$$

This equation exhibits only the final result, the chemical change itself being more complicated.

90. Properties.—Ethylene is a colorless gas, unfit for breathing and having a sweet ethereal odor. It readily ignites and burns with a bright luminous flame that evolves considerable quantities of smoke. It is soluble in about eight times its volume of water, and slightly soluble in alcohol and water. It liquefies at $-1.1°$ C. and at a pressure of 43 atmospheres or at $-103°$ C. at ordinary pressure. When mixed with 3 volumes of oxygen, it explodes violently upon coming in contact with a flame. It is decomposed by the electric spark, the carbon being deposited and twice its volume of hydrogen remaining. Ethylene unites directly with an equal volume of chlorine to form an oily liquid of the composition $C_2H_4Cl_2$:

$$C_2H_4 + Cl_2 = \underset{\text{dichlorethane}}{C_2H_4Cl_2}$$

ACETYLENE

Formula C_2H_2. Molecular weight 26.026

91. History and Preparation.—Acetylene was discovered by E. Davy in 1836, and investigated by Berthelot in 1860. It is produced during the combustion of many hydrocarbons in a limited supply of air; thus, when a Bunsen burner lights at the bottom of the tube, acetylene is produced in considerable quantities. It may be prepared by the direct union of carbon and hydrogen at high temperature. The most convenient method of preparing the gas is by passing a current of electricity from a powerful voltaic battery through two electrodes of carbon enclosed in a glass flask containing hydrogen. It is now extensively used as an illuminating gas, being prepared by the action of water on calcium carbide as follows:

$$\underset{\text{calcium carbide}}{CaC_2} + \underset{\text{water}}{2H_2O} = \underset{\text{calcium hydroxide}}{Ca(OH)_2} + \underset{\text{acetylene}}{C_2H_2}$$

92. Properties.—Acetylene is a colorless, poisonous gas, with a pleasant ethereal odor when pure, but when mixed with impurities it has a peculiar and disagreeable odor. It is condensable to a liquid under a pressure of 68 atmospheres at 37° C. It is a non-supporter of combustion and burns with a bright, luminous, but rather smoky flame. It is quite soluble in water, and is also readily absorbed by ammoniacal cuprous chloride, forming a red precipitate of cuprous acetylide, Cu_2C_2, that is explosive. This explosive body is sometimes formed in brass gas pipes by the action on them of the acetylene in coal gas, and which may have been the cause of fatal accidents.

93. Welding and Cutting.—Within recent years the welding and cutting of steel and other metals by means of the oxyhydrogen and oxyacetylene blow torch has become common practice. Each flame has its own particular advantages and field of application, due to the existing difference in their temperatures. The temperature of the oxyhydrogen flame is about 2,000° C.; that of the oxyacetylene flame is about 2,400° C.

For welding thin sheets of metal, special metal alloys, or aluminum, copper, lead, or brass, the oxyhydrogen flame is often preferable to the oxyacetylene flame. This is because of the fact that with the high temperature of the oxyacetylene flame, it is easier to burn these metals than it is with the oxyhydrogen flame, the temperature of which is much lower. For heavy welding work, however, oxyacetylene flame excels.

For cutting iron or steel, the oxyhydrogen flame is more efficient than the oxyacetylene flame. This may be easily understood from an examination of the products of combustion of the gases involved.

As the mixture of the gases comes from the blow torch and is ignited, the product of combustion in the case of the oxyhydrogen flame is water vapor:

$$\begin{array}{ccccc} 2H_2 & + & O_2 & = & 2H_2O \\ \text{2 volumes} & + & \text{1 volume} & = & \text{2 volumes} \end{array}$$

while in the case of the oxyacetylene flame the products are,

$$\begin{array}{ccccccc} 2C_2H_2 & + & 5O_2 & = & 4CO_2 & + & 2H_2O \\ \text{2 volumes} & + & \text{5 volumes} & = & \text{4 volumes} & + & \text{2 volumes} \end{array}$$

The gases immediately at the point where the metal is being cut are diluted by the products of combustion; the extent of this dilution will greatly affect the burning of the gaseous mixtures and likewise will reduce the efficiency of the cutting flame. Thus, in the case of the oxyhydrogen flame, 2 volumes of gaseous combustion products are given off, while in the case of the oxyacetylene flame, 6 volumes of combustion products will act to dilute the gas. Obviously, therefore, the efficiency of the oxyacetylene flame as a cutting agent, especially in heavy work, will be reduced below that of the oxyhydrogen flame.

CYANOGEN

Formula C_2N_2. Molecular weight 52.026

94. History and Preparation.—Cyanogen was discovered by Gay-Lussac in 1815; being the first compound radical isolated, its discovery marks an era in the science of theoretical chemistry, and to a still greater extent in that of

organic chemistry. Its name is derived from a Greek word meaning *blue,* in allusion to the fact that it is an important constituent of the well-known pigment Prussian blue, $Fe_4[(FeCN)_6]_3$, then known as prussiate of iron, from which Gay-Lussac first obtained it. Cyanogen can be obtained by heating the cyanide of gold, silver, or mercury:

$$Hg(CN)_2 = Hg + C_2N_2$$

95. Properties.—Cyanogen is a colorless gas, exceedingly poisonous, possessing a strong odor of bitter almonds. Its specific gravity is 1.806. It may be easily condensed by a pressure of 4 atmospheres or at a temperature of $-25°$ C. to a colorless, highly refractive liquid, which has a specific gravity of .866 and freezes at $-39°$ C. to a transparent, icelike solid. On contact with flame cyanogen readily takes fire and burns with a characteristic pink flame edged with green, yielding carbon dioxide and nitrogen. Free, or molecular, cyanogen is composed of two of the cyanogen radicals, CN, $(CN)_2$, being analogous to Cl_2. Moreover, the cyanogen radical acts precisely like an elemental monad, forming compounds corresponding to the chlorides, thus: Potassium chloride, KCl; hydrochloric acid, HCl; hypochlorous acid, $HClO$; potassium cyanide, KCN; hydrocyanic acid, HCN; cyanic acid, $HCNO$.

ILLUMINATING GAS

96. History and Preparation.—The production of a combustible gas from coal was first observed by Clayton in 1727, although it was not until 1792 that the application of this gas as a means of illumination was successfully carried out by Murdock. In 1802 he lighted with gas Boulton & Watt's works at Soho near Birmingham, in England. The streets of London were first lighted with gas in 1812, while Paris did not adopt this method of illumination until 1815.

Illuminating gas is manufactured by the destructive distillation of bituminous coal, although various other products such as petroleum, wood, resin, etc., have also been used. The general interior arrangement of a gasworks for the manu-

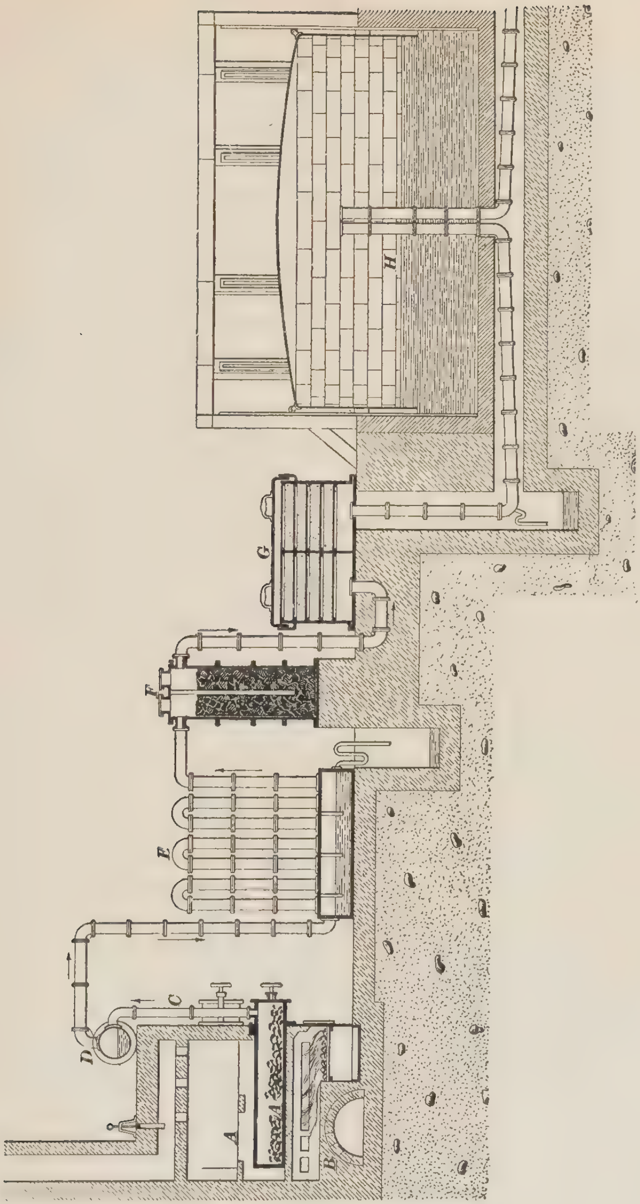


FIG. 5

facture, purification, and collection of coal gas is shown in Fig. 5. The coal is placed in cylindrical iron retorts *A* set in a furnace *B*. As a rule, five retorts are heated by the same fire, such a set of retorts being technically known as a *bench*. The products of the destructive distillation pass from the retort through a tube *C* into a larger horizontal tube *D*, known as the hydraulic main; here the tar and a portion of the water are condensed to liquids. The gas then passes through a series of vertical pipes *E*, and then through the coke box *F* —technically known as the scrubber—by which it is still further cooled and the condensable vapors separated. It finally enters the purifier *G*, which consists of a large metallic box containing on shelves for this purpose either dry slaked lime, or, what is preferable, ferric hydroxide mixed with lime and sawdust. From this purifier the gas issues freed from most of its impurities such as sulphur compounds and carbon dioxide in particular, and is collected in the gasholder *H* for distribution.

97. Composition and Properties.—Coal gas is a mixture of several gaseous products that vary according to the quality of the coal employed in its manufacture, the temperature at which it is distilled, etc. It consists essentially of hydrogen and methane mixed with variable proportions of ethylene, acetylene, carbon monoxide, carbon dioxide, nitrogen, oxygen, and hydrogen sulphide. Its specific gravity is about .4 and increases with the illuminating value of the gas.

The illuminating value of a gas is determined by an instrument called a photometer, in which the amount of light given by the gas burning from a jet at the rate of 5 cubic feet per hour is compared with that emitted by a standard candle burning 120 grains of spermaceti in the same time. Coal gas may under favorable circumstances rise in its illuminating power as high as 25 to 30 candles, although the average coal gas supplied in our cities rarely amounts to 16 candlepower.

98. The constituents that contribute most largely to the illuminating value of the gas are acetylene, ethylene, the vapor of benzene, and similar hydrocarbons. The most objectionable constituent is sulphur, which is present as hydrogen sulphide

and carbon disulphide; this is converted by combustion into sulphurous and sulphuric acids, which seriously injure furniture, pictures, etc. The object of the manufacturer of coal gas is to remove as far as possible everything except the essential constituents and at the same time to obtain as large a volume of gas from a given weight of coal as is consistent with good illuminating value.

The collateral products of the coal-gas manufacture are in general two—the ammoniacal liquor and the gas tar. The former consists of the condensed water holding in solution the ammonia produced from the nitrogenous substances in the coal; the latter is very complex, containing in its lighter portions certain volatile liquids as benzene and toluene and certain volatile alkaline bases such as aniline and chinoline, and in its heavier portions certain phenols as phenol proper (carbolic acid) and cresol; and certain hydrocarbons, as naphthalene and anthracene. All these collateral products, as well as the destructive distillation of coal, are more minutely treated in the Sections on organic chemistry.

CALCIUM CARBIDE

Formula CaC_2. Molecular weight 64.08

99. Preparation.—Calcium carbide is formed when lime and carbon are mixed in the proper proportions and heated to a high temperature. The lime is reduced and the metallic calcium unites with the carbon to form the carbide:

$$CaO+3C=CaC_2+CO$$

The reaction is carried out in an electric furnace.

Calcium carbide is sent to the market in steel barrels, steel drums, or in tin cans, in the form of grayish-black lumps. As previously stated, this material is extensively used in the manufacture of acetylene.

CARBORUNDUM OR SILICON CARBIDE

Formula SiC. Molecular weight 40.305

100. Preparation.—When sand or silica, SiO_2, is heated in an electric furnace with an excess of carbon, silicon carbide or carborundum is formed:

$$SiO_2+3C=SiC+2CO$$

This material is extensively used as an abrasive.

CARBON BISULPHIDE

Formula CS_2. Molecular weight 76.125

101. History and Preparation.—Carbon bisulphide, also called carbon disulphide, was discovered by Lampadius in

Fig. 6

1796. It is found in small quantities among the products of the destructive distillation of coal. It is formed like the dioxide by the direct union of its elements. It is prepared on a large scale by passing the vapor of sulphur over red-hot charcoal, the elements uniting according to the following equation:

$$C+2S=CS_2$$

102. Carbon bisulphide may be prepared on a small scale in the laboratory by means of the apparatus shown in Fig. 6. The combustion tube, which should be about 2 feet long, is filled for about 3 inches from the sealed end with small pieces of sulphur; the rest of the tube is filled with small pieces of charcoal. The open end of the tube is connected with a glass tube dipping

below the surface of water in a bottle placed in ice water. The charcoal is heated to redness first and then the part containing the sulphur is heated. The sulphur vapor passes over the red-hot charcoal, combines with the carbon, and is deposited under the water in the receiver. The excess of sulphur and the water are removed by distilling on a water bath.

On a large scale, an upright cast-iron cylinder from 10 to 12 feet long and about 2 feet in diameter, and provided with a lid to admit of charging with charcoal, is used. The cylinder has a hopper near the bottom for the purpose of introducing the sulphur. The whole is heated from below. The sulphur vaporizes, combines with the red-hot carbon, forming carbon bisulphide which is condensed in a long iron tube and collected under water in an iron basin. The impure material is then purified by distillation. Within recent years carbon bisulphide has been made on the large scale in the electric furnace, and in the United States, at least, this process has practically displaced the older one, since the furnace operates automatically and the process is continuous.

103. The furnace consists of two upright cylinders, one within the other. The inside compartment is filled with charcoal and the compartment which surrounds it contains the sulphur. At the bottom the two cylinders unite in a common hearth and the sulphur and charcoal come in direct contact. The electrodes pass in through the hearth and into the compartment containing the charcoal. When the current is turned on, the furnace becomes hot and the sulphur begins to melt and vaporize. The vapors pass up through the hot charcoal and react when a region of proper temperature is reached. The carbon bisulphide vapors escape from the top of the furnace and are condensed.

104. Chemical Properties.—Carbon bisulphide is a very inflammable liquid, taking fire in the air at a temperature of 150° C. and burning with a blue flame. The decomposition produces carbon and sulphur dioxide, as follows:

$$CS_2+2O_2=C+2SO_2$$

A mixture of carbon-bisulphide vapor and oxygen forms an explosive mixture even when the mixture is thoroughly dry. The vapor of carbon bisulphide is poisonous when inhaled in large quantities, its effects showing symptoms very similar to those of hydrogen sulphide poisoning. Carbon-bisulphide vapor burns in nitric oxide with an intensely brilliant blue flame. Carbon bisulphide is only slightly soluble in water, but mixes with alcohol and ether in all proportions.

Carbon bisulphide is used in the industries as a solvent for caoutchouc, oils, and fats, and frequently it is employed for extracting the essential oils that contain the perfumes of roses, lavender, jasmine, etc. It also dissolves sulphur, phosphorus, and iodine, and is used to determine the moisture in commercial iodine. It is also used frequently as a starting point in the synthetic preparation of the hydrocarbons, because if mixed with hydrogen sulphide and passed over copper filings heated to redness, methane is produced, thus:

$$CS_2+2H_2S+4Cu=4CuS+CH_4$$

When carbon bisulphide is dissolved in alcohol and with the aid of heat is acted on by ammonia, ammonium sulphocyanide is formed, according to the equation:

$$CS_2+2NH_3=H_2S+NH_4CNS$$

105. Physical Properties.—Carbon bisulphide is a colorless, mobile, brilliant, strongly refractive liquid that when perfectly pure possesses an agreeable ethereal odor resembling that of chloroform. Its specific gravity is 1.29. It may be frozen to a solid which melts at −110° C.; it boils at 46.2° C., yielding a dense vapor. It is very volatile, evaporates rapidly in the air, and produces great cold.

CARBON OXYSULPHIDE

Formula COS. Molecular weight 60.065

106. Preparation.—Carbon oxysulphide, COS, is formed when a mixture of carbon monoxide and sulphur vapor is passed through a moderately heated tube or is subjected to the

action of electric sparks. It is usually prepared by heating potassium sulphocyanide gently with dilute acids. The potassium sulphocyanide is first broken up into sulphocyanic acid:

$$KCNS+H_2SO_4=HCNS+KHSO_4$$

and the sulphocyanic acid is then decomposed by the water of dilution, thus:

$$HCNS+H_2O=NH_3+COS$$

In practice, however, sufficient sulphuric acid is added to unite with the ammonia gas and form ammonium sulphate, thus:

$$KCNS+2H_2SO_4+H_2O=COS+KHSO_4+NH_4HSO_4$$

107. Properties.—Carbon oxysulphide is a colorless gas with a peculiar odor somewhat resembling that of carbon disulphide. It has a specific gravity of 2.11, and is very inflammable, burning with a bright blue flame to carbon dioxide and sulphur dioxide. It is rapidly absorbed by aqueous or alcoholic solutions of caustic potash, yielding the carbonate and sulphide of potassium:

$$COS+4KOH=K_2S+K_2CO_3+2H_2O$$

CARBON TETRACHLORIDE

Formula CCl_4. Molecular weight 153.845

108. Preparation.—Carbon tetrachloride is prepared by passing dry chlorine into carbon bisulphide containing a little dissolved iodine. The latter acts as a catalytic agent.

$$3Cl_2+CS_2=S_2Cl_2+CCl_4$$

As will be seen from the equation, sulphur monochloride, S_2Cl_2, is also formed, but because of the great difference in their boiling points (CCl_4, 76.74° C.; S_2Cl_2, 138° C.) one compound may be readily separated from the other by fractional distillation.

109. Properties.—Carbon tetrachloride is a heavy, water-white liquid having a specific gravity of 1.5817, and boiling at 76.74° C. Carbon tetrachloride is non-inflammable

and for this reason it may be used advantageously as a solvent in the fat and oil industries. Gasoline and benzine vapors are very inflammable and the use of these liquids as solvents is constantly attended by a risk. Mixtures of carbon tetrachloride and benzene are used considerably as cleaning agents and several fire extinguishers are now found on the market which employ carbon tetrachloride as the extinguishing medium.

COMBUSTION

110. Definition.—The definition generally given and accepted for the term *combustion* is as follows: *Combustion is a process of oxidation accompanied by the development of light and heat.* This definition implies that the element oxygen is the active agent which either supports combustion or causes combustion to take place. The term combustion, however, is used rather loosely and has been applied to chemical reactions which take place with the development of light and heat although oxygen is not present; the combustion of chlorine in hydrogen, the combustion of a metal in chlorine, etc., are typical instances.

In this discussion, however, the application of the term combustion will be limited to those reactions in which oxygen takes part.

111. Combustibles.—It is evident that at least two substances must be concerned in every combustion—the combustible, that is, the body that burns; and the supporter of combustion, that is, the gas in which the combustion takes place. Those substances that serve as combustibles are naturally very numerous. The illuminating gases and the different varieties of coal have already been mentioned.

112. Of liquids, the vegetable oils known as rape, olive, and turpentine, the animal oils called sperm and lard, and the mineral oils derived from petroleum may be quoted. Of solids from the vegetable kingdom, wood and bayberry wax; from the animal, tallow and its product, stearin; and from the mineral, paraffin and the various sorts of coal are examples. All

these substances, though so different in character and origin, are alike in the respect that they contain carbon and hydrogen. Some contain oxygen in addition.

113. Heat of Combustion.—Not only do substances give out heat in burning, but the amount of heat evolved by the combustion, or combination with oxygen, of a given weight of any pure substance, is always the same and it may be measured, as will be shown. Thus, whether the substance be burned slowly or rapidly, provided it is burned to the same products of combustion, the total amount of heat generated never varies. Table IV gives the number of heat units evolved by combustion in oxygen of 1 gram of each substance. A heat unit is the quantity of heat necessary to raise 1 gram of water from 0° to 1° and this unit is called the calorie.

TABLE IV

HEAT DEVELOPED DURING COMBUSTION

Substance	In Oxygen Heat Units (Calories)
Hydrogen	34,462
Carbon	8,080
Sulphur	2,220
Phosphorus	5,747
Carbon monoxide	2,634
Methane	13,063
Ethylene	11,942
Alcohol	6,909

Of the elements, hydrogen develops by far the greatest amount of heat on combustion; the next greatest amount is developed by carbon. Of the various compounds of carbon, carbon monoxide, during its further combustion to carbon dioxide, evolves a considerable quantity of heat.

114. It is interesting to compare the amount of heat evolved in the two stages of the combustion of carbon, namely from carbon to carbon monoxide and then to carbon dioxide.

$$2C+O_2=2CO$$
$$2CO+O_2=2CO_2$$

Molecular weight $2C \quad =24$

Molecular weight $O_2 \quad =32$

Molecular weight $2CO=56$

From the first equation and the molecular weights it may be calculated that 1 gram carbon yields:

$$24:1::56:x$$
$$24x=56$$
$$x=\frac{56}{24} \text{ grams of carbon monoxide}$$

From Table IV, the combustion of 1 gram of carbon monoxide to carbon dioxide evolves 2,634 calories, therefore $\frac{56}{24}$ grams of carbon monoxide will evolve:

$$2{,}634\times\frac{56}{24}=6{,}146 \text{ calories}$$

115. But according to Table IV, the total number of calories evolved by the complete combustion of carbon is 8,080. Therefore, 1 gram of carbon evolves in oxidation to the monoxide $8{,}080-6{,}146=1{,}934$ heat units, and during further oxidation to the dioxide, 6,146 heat units. It has already been shown that when the carbon dioxide formed in a fire of carbon passes upwards through red-hot carbon it is reduced to the monoxide, which in turn burns on the upper surface of the fire where there is free access to air. Whenever carbon is burned with a limited supply of oxygen as where a draft of air is drawn through a furnace containing large quantities of coke or other forms of carbon, the monoxide is the chief product of combustion. This cannot burn until it reaches the air. Accordingly in the older forms of furnaces used in metallurgical operations, particularly the blast furnace used for the smelting of iron ores, enormous quantities of carbon monoxide were formed and allowed to burn to waste on the tops of the furnaces. The value of this gas as a fuel is now recognized and it is consequently drawn from the upper part of the furnaces and utilized for heating purposes.

116. Temperature of Combustion.—Although the absolute amount of heat evolved by the combustion of a unit weight of hydrogen, for instance, is always the same, the temperature produced may vary within certain limits. Thus, first of all, if within a given space hydrogen is caused to burn in one instance at twice the rate of another, it follows that as a

greater number of units of heat are evolved in the same period of time, the temperature of that space will be raised proportionately higher. Other causes also influence the temperature produced by combustion; for example, a jet of hydrogen burning the same number of cubic feet per hour, produces a much higher temperature when it burns in oxygen than it does when burning in air.

If 2 grams of hydrogen are burned in oxygen, the heat evolved must raise the temperature of the 17.88 grams of water produced. But if the oxygen is obtained from air, not only must the 15.88 grams of oxygen in the water produced be heated, but also the 63.52 grams of nitrogen with which the oxygen was mixed.

$$\underset{2g}{\frac{4}{2H_2}} + \underset{x_1}{\frac{31.76}{O_2}} = \underset{x}{\frac{35.76}{2H_2O}}$$

$$\frac{4}{2} = \frac{35.76}{x}$$

$$x = 17.88 \text{ g. water}$$

and

$$\frac{4}{2} = \frac{31.76}{x_1}$$

$$x_1 = 15.88 \text{ g. oxygen}$$

Air consists of $\frac{1}{5}$ oxygen and $\frac{4}{5}$ nitrogen. Therefore a quantity of air containing 15.88 grams oxygen, will also contain 63.52 grams nitrogen. The same number of units of heat is in the one case spread over 17.88 grams; in the other, over 17.88+63.52 =81.4 grams of gaseous matter—from which it follows that the temperature in the first instance must be very much higher than in the second.

117. Combustion of Methane, Acetylene, and Ethylene.—The combustion of these three bodies affords some very interesting and instructive examples of the laws of combination by volume. Subjoined are the molecular equations representing the reactions that occur, together with equations of some other familiar examples of combustion:

$$\underset{\text{1 volume}}{CH_4} + \underset{\text{2 volumes}}{2O_2} = \underset{\text{1 volume}}{CO_2} + \underset{\text{2 volumes}}{2H_2O}$$

$$\underset{\text{2 volumes}}{2C_2H_2} + \underset{\text{5 volumes}}{5O_2} = \underset{\text{4 volumes}}{4CO_2} + \underset{\text{2 volumes}}{2H_2O}$$

$$\underset{\text{1 volume}}{C_2H_4} + \underset{\text{3 volumes}}{3O_2} = \underset{\text{2 volumes}}{2CO_2} + \underset{\text{2 volumes}}{2H_2O}$$

$$\underset{\text{2 volumes}}{2CO} + \underset{\text{1 volume}}{O_2} = \underset{\text{2 volumes}}{2CO_2}$$

$$\underset{\text{2 volumes}}{2H_2} + \underset{\text{1 volume}}{O_2} = \underset{\text{2 volumes}}{2H_2O}$$

$$\underset{\text{1 volume}}{H_2} + \underset{\text{1 volume}}{Cl_2} = \underset{\text{2 volumes}}{2HCl}$$

These equations show to a nicety the relation that exists between the volumes of gases and the respective volumes of oxygen required for their combustion. They afford additional illustrations of the method of deducing these quantities from molecular equations.

As gaseous molecules are assumed (at the same temperature and pressure) to occupy the same space, it follows that the number of molecules of any gas participating in a chemical change represents the number of volumes of the gas concerned.

118. General Method of Determining Heat Units. The apparatus used for the purpose of determining the heating value of coals and other combustibles, is called a bomb calorimeter. It consists essentially of a strong steel receptacle (the bomb proper) into which the weighed sample of the combustible material is placed and within which it is completely burned. To insure complete combustion, the sample to be burned is always prepared in a finely divided condition and kept in contact with oxygen under high pressure.

The sample in the bomb is ignited by means of a fuse wire which dips into it and is heated to incandescence by passing an electric current through it. During the period of combustion the bomb is entirely immersed in a known quantity of water which has been brought to a constant temperature and the rise in temperature of the water caused by the combustion is accurately measured.

From the data obtained, the heating value of the coal, etc. can be calculated. Details of the method used will be given in the Sections treating on the subject of quantitative analysis.

COMBINATION OF OXYGEN WITH HEATED GASES

COMBUSTION

119. Structure of Flame.—A **flame** is defined as a hot gas combining with oxygen at a temperature at which it becomes visible; that is, until it emits light. Some substances like sulphur and phosphorus give a flame when burned in air or in other gas, such substances being converted into gases or vapors at the temperature of combustion. The presence of a combustible gas or vapor is one of the conditions necessary for the existence of the flame. Thus, pure carbon burns without a flame and only becomes incandescent, because it is non-volatile. Similarly, a diamond or a piece of charcoal will burn in oxygen with a steady glow but without flame, because it cannot be converted into vapor.

FIG. 7

120. To obtain a brilliant light from a flame, it is essential that it should contain particles that are capable of incandescence when highly heated. The flame of an oxy-hydrogen blowpipe is very pale but when the flame is made to heat a column of lime an intense light is obtained, due to the lime being heated to incandescence.

Phosphorus when burning emits a very luminous flame, owing to the fact that the oxide formed in the combustion is heated to incandescence.

From these statements it can be seen that the incandescent matter must not necessarily be a product of the combustion, as any solid in a finely divided state will give illuminating power to a flame. If finely divided carbon is blown into a hydrogen flame from a bottle arranged as shown in Fig. 7, the flame will be rendered highly luminous. The luminosity of most flames is due to the presence of highly heated carbon.

Hydrogen and methane give pale flames because they burn directly to carbon dioxide and water; on the other hand, ethylene and other hydrocarbons burn with a bright flame because at the temperature of combustion they decompose into methane and carbon, and the particles of carbon become incandescent when intensely heated.

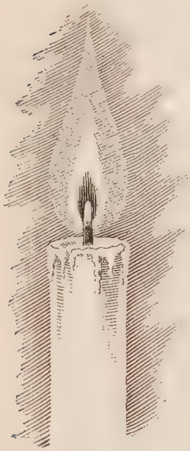


Fig. 8

121. Candle Flame.—When a candle is lighted a portion of the wick burns until the heat reaches the wax which melts and is drawn up into the wick and decomposed into hydrocarbons, which ignite, combine with the oxygen of the air, and produce the flame. The flame in turn melts more of the wax around the wick and the process just described is repeated.

The structure of a candle flame is common to all flames obtained by the combustion of a gas. The flame of a candle consists of three cones, as shown in Fig. 8. The inner cone, which appears black, contains the unaltered gases. These cannot burn because of the absence of air. The presence of unburned gases in this center cone can be shown by holding one end of a glass tube in this cone, when the gases pass through the tube and are ignited at the other end as shown in Fig. 9. In the middle, or luminous, cone an imperfect combustion takes place. The gases break down, some burning completely, and the free carbon is heated to incandescence and gives luminosity to this

Fig. 9

part of the flame. The carbon is not burned, owing to the lack of oxygen sufficient for its combustion. The presence of free carbon in this cone is shown by lowering a porcelain plate on the cone, when a black film of soot will be deposited. The outer cone, or mantle, of the flame is very feebly luminous. In this cone, which is surrounded by air, the separated carbon burns completely and the cone is termed the cone of perfect combustion.

The bright-blue cup surrounding the base of the flame is formed by the perfect combustion of a small portion of the hydrocarbons. Owing to the plentiful supply of air at this point, there is no separation of carbon.

122. Argand Burner.—As has been stated, all gas flames possess an identical structure and by proper attention to the supply of air, a flame fitted for either heating or illuminating can be obtained.

For illuminating purposes the best results are obtained by what is known as the Argand burner shown in Fig. 10. Air is admitted to the gaseous center of a ring-shaped flame, and the addition of a chimney to produce a draft insures great brilliancy and steadiness of the flame. In recent years a more brilliant flame for illuminating purposes is obtained by employing the heat of combustion for heating to incandescence an open-meshed mantle impregnated with a mixture of rare earths.

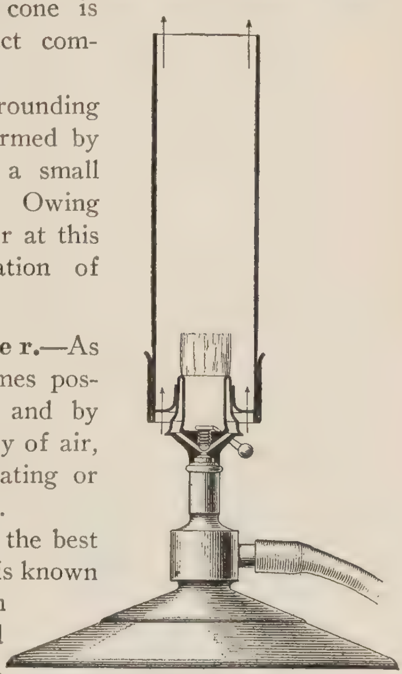


Fig. 10

123. Bunsen Burner.—An excellent burner for heating purposes is the Bunsen burner shown in Fig. 11. This consists of a gas tube *a* projecting into the large mixing tube *b*. Air enters through the openings *c* at the base of the burner,

which are closed or opened by turning the collar *d*, thus regulating the supply of air. When a good supply of gas is turned on a quantity of air about double the volume of gas is drawn in through the openings *c*, and the flame obtained by igniting the gaseous mixture at the orifice of the wide tube *b* affords an intense heat but no luminosity. If the air holes are closed, a luminous flame is obtained. The non-luminous flame contains an excess of oxygen and is used for oxidizing purposes, hence is known as an oxidizing flame. The luminous, or reducing, flame, is, as its name implies, reducing in its action, the glowing carbon in it abstracting oxygen from substances containing it.

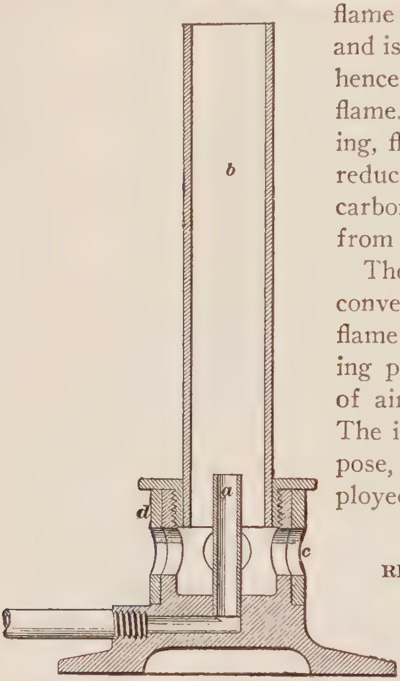


Fig. 11

The luminous flame may be converted into a non-luminous flame possessing considerable heating powers by blowing a current of air from a jet into the flame. The instrument used for this purpose, termed a blowpipe, is employed extensively in assaying.

REMOVAL OF COMBUSTION PRODUCTS

124. Ventilation. Pure air may be defined as air composed of nitrogen, oxygen, and carbon dioxide (about 3 parts in 10,000), together with water vapor, ammonia, and hydrogen dioxide, but nothing of an injurious nature. The most common cause of contamination of air is the combustion products of gas flames and the expiration products of human beings in rooms which have an inadequate supply of fresh air. The air from the lungs of a human being at each expiration contains from 3 to 4 parts of carbon dioxide in each 100 parts of air, this gas being produced by the combus-

tion process taking place in the lungs. This amount could not be breathed again without danger, hence the necessity for a continued supply of fresh air to dilute the carbon dioxide sufficiently to render it harmless. The natural processes of respiration tend to raise the temperature of the air, thus causing it to expand and diminish its specific gravity, and causing it to ascend and give place to fresh air. In order to remove the vitiated air, a means of escape near the ceiling should be provided.

125. The principles of ventilation are usually illustrated by means of the apparatus shown in Figs. 12, 13, and 14. If

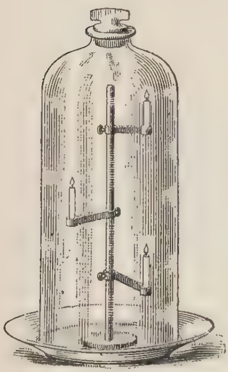


Fig. 12

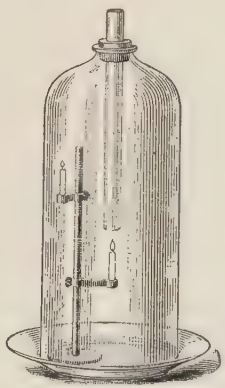


Fig. 13

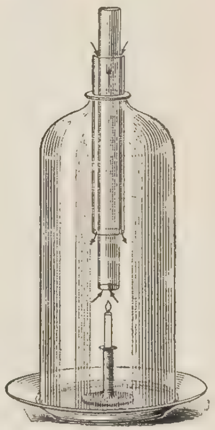


Fig. 14

lighted candles held at different heights are covered with a bell jar, as in Fig. 12, the warm carbon dioxide formed by the burning candles will accumulate in the upper part of the bell jar and gradually extinguish the candles, the upper one first. If, however, a glass tube is placed in the neck of the bell jar so that the inner end is just slightly above the lower candle, as shown in Fig. 13, both candles will be extinguished. If the bell jar is raised slightly so as to allow air to enter, the upper candle will go out and the lower one will continue to burn. The air entering under the jar will replace the carbon dioxide formed, which will pass out through the tube. The

same result can be accomplished by placing two tubes one within the other in the neck of the bell jar, Fig. 14. The products of combustion escape through the center tube and fresh air enters through the space between the tubes and the candle continues to burn.

126. The Miner's Safety Lamp.—Davy discovered the fact that flame if cooled below a certain point is extinguished; hence, no flame can be propagated through a cold, fine metal tube.

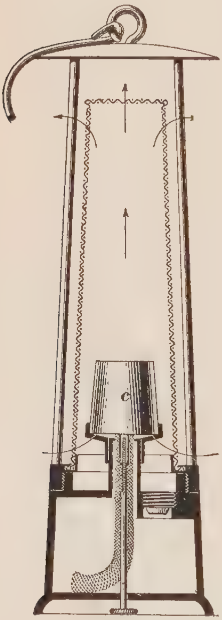


Fig. 15

Thus wire gauze, being a collection of small, short, metallic tubes, will consequently not allow the passage of flame and when pressed on a gas flame will depress it in the same way as if it were a solid plate. If the gauze is held 2 inches above the jet, the gas may be lighted above the gauze, but the flame will not pass through to the jet. With two pieces of gauze, the gas may be made to burn between them, but neither above the upper nor below the lower; or, the gas may be made to burn above and below, but not between them.

The miner's safety lamp, generally known as Davy's safety lamp, is based on this discovery. It is represented in section in Fig. 15, and consists of a metallic lamp, the wick of which is surrounded with wire gauze enclosed in a frame, by which the whole may be suspended. The explosive mixture of air with the gases developed in the mines can, of course, enter the gauze and burn within the gauze enclosure, but the flame cannot pass outwards through the gauze, since it is cooled and consequently extinguished; hence, such a lamp prevents the explosion of these dangerous gases.

INORGANIC CHEMISTRY

(PART 6)

THE HALOGENS

1. Introduction.—In this Section the four closely related elements, chlorine, bromine, iodine, and fluorine, will be studied. These elements are called the *halogens*, from the Greek works *hals* and *gennao*, which mean, literally, *I produce salt.*

Of these elements, chlorine, bromine, and iodine are more closely related to one another than they are to fluorine. Chlorine, bromine, and iodine are usually found together in nature, but fluorine seldom accompanies them. When the first three elements are found together in nature, chlorine is usually present in the largest quantity, bromine next, and iodine in the smallest quantity. Of these elements, fluorine and chlorine are gases, bromine a liquid, and iodine a solid, under ordinary conditions. Fluorine does not combine with oxygen, but the other members of this group unite with it in a number of proportions.

These elements form some compounds among themselves; for example, iodine forms the compounds IBr, ICl, ICl_3, and IF_5. The halogens unite with hydrogen and form the compounds hydrochloric acid, HCl, hydrobromic acid, HBr, hydriodic acid, HI, and hydrofluoric acid, HF. The first three are gases, while hydrofluoric acid is a volatile liquid; all have strong acid properties. They combine with metals and form salts known as the *halides* In combination with each other, and with other non-metallic elements, the valence of these elements varies; but toward the metals they appear to be monovalent.

CHLORINE

Symbol Cl. Atomic weight 35.46. Molecular formula Cl_2. Molecular weight 70.92.

2. History.—Chlorine was discovered in 1774 by Scheele, who called it dephlogisticated muriatic acid, a name which was afterwards changed by Berthollet to oxymuriatic acid. It was first recognized as an element in 1809 by Gay-Lussac and Thenard and in 1810 by Sir Humphry Davy, who gave it the name by which it is now known.

3. Occurrence.—Chlorine is not found in a free state in nature, but many of its compounds, especially the chlorides of sodium, magnesium, potassium, and calcium, are abundant in the mineral world. Sodium chloride, or common salt, is found in large quantities in sea-water and in the residual deposits left where sea-water has evaporated to dryness. It is generally accompanied by the chlorides of magnesium and potassium. At Stassfurt, Germany, the strata of these residual deposits are over 1,000 feet in thickness. Some chlorides are also found in the atmosphere wherever there are bodies of salt water.

4. Laboratory Preparation.—Chlorine is easily made in the laboratory by warming manganese dioxide, MnO_2, with concentrated hydrochloric acid, HCl. Two distinct changes enter into the process. In the first one, manganic chloride and water are formed; thus:

$$MnO_2+4HCl=MnCl_4+2H_2O$$

The manganic chloride is, however, unstable and breaks up into manganous chloride and chlorine; thus:

$$MnCl_4=MnCl_2+Cl_2$$

For reasons of economy, sodium chloride and sulphuric acid are sometimes used instead of hydrochloric acid, as they form hydrochloric acid during the preparation of chlorine; thus:

$$MnO_2+4NaCl+3H_2SO_4=2NaHSO_4+Na_2SO_4+MnCl_2 +2H_2O+Cl_2$$

The products of this reaction have, of course, been analyzed and have been found to be as represented by the equation.

5. It may be noted that the change between manganese dioxide and hydrochloric acid is representative of a change that is general; that is, when an acid reacts in the proper proportions with the oxide of a metal, the oxygen of the oxide unites with the hydrogen of the acid to form water and the metal of the oxide combines with the acid radical of the acid. In this case, the oxygen in combination with the metal maganese unites with the hydrogen in the hydrochloric acid to form water

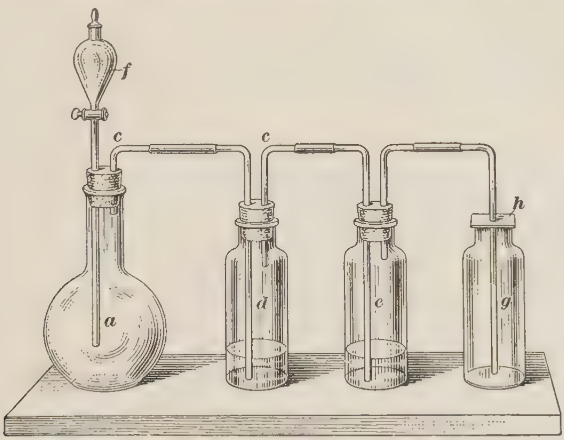


Fig. 1

and the metal manganese combines with the acid radical chlorine of the hydrochloric acid.

The best way to make chlorine in the laboratory is by treating potassium permanganate, $KMnO_4$, with concentrated hydrochloric acid that has been diluted with one-third its volume of water. The change that takes place in this case is:

$$2KMnO_4+16HCl=8H_2O+2KCl+2MnCl_2+5Cl_2$$

Apparatus arranged as is shown in Fig. 1 is used to prepare chlorine by the method described. In this method, which has been found to give satisfactory results, 10 grams of manganese dioxide, 22 grams of sodium chloride, and 40 cubic centimeters of sulphuric acid (made by adding slowly and

with stirring 12 cubic centimeters of concentrated sulphuric acid to 28 cubic centimeters of water) are placed in the flask *a*. The cork holding the separatory funnel *f* (which is kept closed) and the delivery tube *c* is placed in the neck of the flask. A wash-bottle *d* containing water removes any hydrochloric acid that may pass over with the chlorine. A wash-bottle *e* containing sulphuric acid dries the chlorine, which is then carried to a collecting cylinder *g*. A cardboard cover *h* is placed over the cylinder to prevent the escape of chlorine into the air. Gentle heat is applied to the flask to accelerate the formation of chlorine.

CAUTION.—Care must be taken to avoid the escape of chlorine. Windows should be open when preparing this gas so as to get proper ventilation. *To inhale chlorine, in quantity, is dangerous, for it produces an inflammation of the lungs and throat.*

6. Commercial Preparation.—Of the many methods formerly used to manufacture chlorine, all have been or are being replaced by electro-chemical methods.

There are two commercial processes for making chlorine electrolytically: (*a*) By the electrolysis of fused sodium chloride and (*b*) by the electrolysis of sodium chloride in an aqueous solution.

(*a*) *Electrolyzing Fused Sodium Chloride.*—Sodium chloride melts at 804° C. and is at this temperature a good conductor of electricity. When an electric current of sufficient voltage is passed through the fused salt, gaseous chlorine is liberated at the anode and liquid metallic sodium at the cathode. The sodium, being lighter than sodium chloride, floats up through the fused material and is then converted to sodium hydroxide, $NaOH$, also called caustic soda. The chlorine is drawn off into collecting compartments by suction.

(*b*) *Electrolysis of an Aqueous Sodium-Chloride Solution.* When an electric current is passed through a solution of sodium chloride (common salt) in water, chlorine collects at the anode and sodium at the cathode. The reactions taking place during this electrolysis are complicated. Most of the chlorine is collected, but a small portion dissolves in the electrolyte and begins to diffuse toward the cathode. The sodium

liberated at the cathode immediately combines with water to form caustic soda and hydrogen; thus:

$$2Na+2H_2O=2NaOH+H_2$$

The caustic soda at once begins to diffuse toward the anode. When chlorine diffusing toward the cathode meets the caustic soda diffusing toward the anode, sodium hypochlorite, $NaClO$, sodium chloride, and water are formed; thus:

$$2NaOH+Cl_2=NaClO+NaCl+H_2O$$

The reactions are still more complicated when both the caustic soda and sodium hypochlorite react further. However, chlorine, caustic soda, and hydrogen are the final products.

7. Physical Properties.—Chlorine is a greenish-yellow gas, having a peculiar, suffocating odor. Inhaled in small amounts it irritates the throat and lungs, and inhaled in larger amounts it produces serious effects. Some relief from these effects can be obtained by inhaling ether or ammonia Chlorine gas is about two and one-half times as heavy as air, having a specific gravity of 2.491. Its solubility in water varies with the temperature of the latter; thus, at 0° C., 10° C., and 30° C., 150, 300, and 180 parts respectively of chlorine are soluble in 100 parts of water. Owing to its solubility it is generally collected by upward displacement of air, though it can be collected above a strong salt solution, in which the gas is not readily soluble.

Chlorine gas may be liquefied, its critical temperature and pressure being 146° C. and 93.5 atmospheres, respectively. Liquid chlorine is now supplied to consumers in steel cylinders. The liquid boils at −33.6° C., and may be frozen to a solid, melting at −102° C.

8. Chemical Properties.—Chlorine is chemically one of the most active of all elements, for it unites directly with many elements and can replace many others in compounds.

It unites with metals with great readiness. If copper in the form of thin strips is placed in chlorine it reacts with evolution of light and heat to produce cupric chloride; thus:

$$Cu+Cl_2=CuCl_2$$

Antimony in powdered form unites with chlorine to produce antimony chloride; thus:

$$Sb_2+3Cl_2=2SbCl_3$$

In like manner all the common metals excepting gold and platinum unite with chlorine to form chlorides.

Chlorine unites with non-metallic elements also. Sulphur, when heated in the presence of chlorine, forms sulphur monochloride, S_2Cl_2; thus:

$$2S+Cl_2=S_2Cl_2$$

It reacts with phosphorus to form either phosphorus trichloride; thus:

$$P_4+6Cl_2=4PCl_3$$

Or, phosphorus pentachloride; thus:

$$P_4+10Cl_2=4PCl_5$$

depending on the amount of chlorine present.

Chlorine does not unite directly with carbon, nitrogen, or oxygen, but can do so indirectly.

Chlorine unites directly with carbon monoxide in the sunlight to form carbonyl chloride, a liquid boiling at 8.2° C., commonly called phosgene; thus:

$$CO+Cl_2=COCl_2$$

9. Chlorine exhibits an especially strong chemical affinity for hydrogen both free and combined. If a jet of hydrogen burning in air is inserted into chlorine, it will continue to burn, forming hydrogen chloride; thus:

$$H_2+Cl_2=2HCl$$

It can also displace elements that are combined with hydrogen, as, for example, in hydrogen sulphide; thus:

$$2H_2S+2Cl_2=4HCl+2S$$

It reacts with the stable substance hydrogen monoxide, or water, with the liberation of oxygen, by first forming hypochlorous acid, which in turn decomposes to form hydrogen chloride and oxygen; thus:

$$H_2O+Cl_2=HCl+HClO$$
$$HClO=HCl+O \text{ (nascent)}$$

As the oxygen liberated from this combination oxidizes organic coloring matter to colorless products, moist chlorine is frequently used as a bleaching agent.

10. The bleaching power of chlorine, which has become of great importance in the cotton and paper trades, depends on the attraction of chlorine for hydrogen. This bleaching action is not possessed by dry chlorine, but requires water to give it the bleaching effect. The action depends on the oxidation of the coloring matter, thus destroying the color by the nascent oxygen of the decomposed water.

Some researches tend to show that the bleaching action of chlorine is not due to oxygen alone but is aided by hypochlorous acid formed when chlorine acts on the moisture in the material to be bleached:

$$Cl_2+H_2O=HClO+HCl$$

Chlorine as a rule has no effect on mineral colors, nor will it bleach black tints produced by carbon. The so-called disinfecting power of chlorine is due to the same property as is its bleaching power. Among the dangerous and offensive products of putrefaction of animal and vegetable matter are hydrogen sulphide, H_2S, ammonia, NH_3, and similar bodies. These are decomposed by chlorine and the unwholesome properties of the air removed; on that account it is valuable as a disinfectant for badly drained and ventilated buildings, etc. At the present time the greater part of the chlorine manufactured is converted into bleaching powder, or calcium hypochlorite. In this form it can be conveniently transported, and the chlorine may be obtained from it as required. Exposure to air effects a partial liberation of its chlorine and the addition of hydrochloric or sulphuric acid effects a complete liberation of the chlorine.

11. Uses of Chlorine.—Dry chlorine will not bleach dry, colored cloth, but if the cloth is wet and brought in contact with chlorine, the coloring matter in the cloth is oxidized to colorless products, in which case the cloth is said to have been bleached. This action is due to the formation of hypochlorous acid, which liberates oxygen. Bleaching by means of chlorine

is resorted to in many industries. As fabrics from vegetable fibers such as straw, flax, and cotton are in their natural colors slightly yellow, chlorine bleaching is often applied to turn them white. Likewise, foods such as dried fruits and flour are bleached by this process.

Chlorine, both free and in compounds from which it is readily liberated, is also used as a disinfectant; that is, a substance which is destructive to bacterial growth.

COMPOUNDS OF CHLORINE

HYDROGEN CHLORIDE, OR HYDROCHLORIC-ACID GAS

Formula HCl. Molecular weight 36.468

12. History.—The aqueous solution of hydrogen chloride is called hydrochloric acid and sometimes muriatic acid. It was known to the alchemists as spirit of salts, but Glauber, in the 17th century, gave it the name of muriatic acid, which is derived from the Latin word *muria*, which means *brine*. The pure hydrochloric-acid gas was first obtained by Priestley in 1772 though it was not until 1810 that its true composition was ascertained by Davy. It occurs in nature in the gases of active volcanoes, in aqueous solutions in the waters of rivers whose source is in volcanic regions, and in the gastric juice of man and of animals.

13. Preparation.—Hydrogen chloride may be formed by the direct union of the elements of which it is composed, in the presence of a strong light. Thus equal volumes of hydrogen and chlorine may be mixed together and if they are kept in the dark no combination takes place. If the moist gases are exposed to a bright light or if a flame is brought to the mouth of the jar containing them, or if an electric spark is passed through the mixture, the gases will suddenly combine with explosive violence. Hydrogen chloride is also formed by the action of chlorine on nearly all hydrogen compounds. It is most satisfactorily and conveniently prepared in the laboratory,

however, by the action of sulphuric acid on sodium chloride. If the reaction takes place at ordinary temperature, the following change occurs:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

This equation shows that 1 molecule of sodium chloride reacts with 1 molecule of sulphuric acid to produce 1 molecule of sodium hydrogen sulphate, also called acid sodium sulphate, or sodium bisulphate, and 1 molecule of hydrogen chloride.

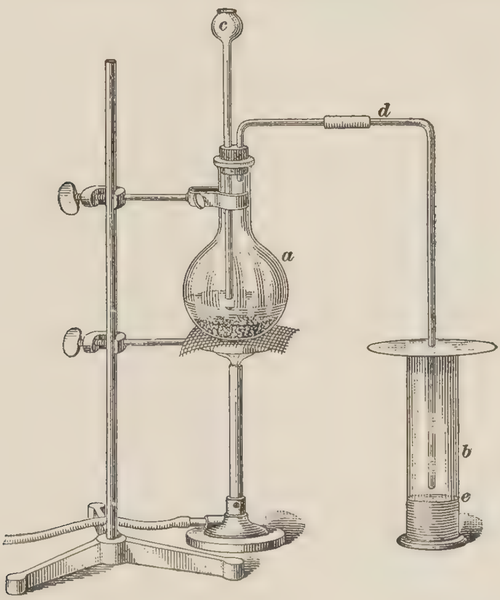


FIG. 2

If a much higher temperature is used, the sodium hydrogen sulphate can react with more sodium chloride to form more hydrogen chloride; thus:

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl$$

or, combining the two changes that occur at the higher temperatures,

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

In this preparation, 15 grams of dry salt are placed in the flask *a*, Fig. 2, and 25 cubic centimeters of sulphuric acid is poured

down through the thistle tube *c*. The flask is then warmed gently. The hydrogen chloride is rapidly given off and is collected by displacement of air in the cylinder *b*. An aqueous solution of hydrogen chloride, which is hydrochloric acid, can be made by passing the hydrogen chloride through a delivery tube *d* that just extends to the surface of the water *e* in the cylinder *b*. The gas readily dissolves in water.

14. Commercial Manufacture of Hydrochloric Acid. Hydrochloric acid is one of the products made in the manufacture of sodium sulphate, which is also known as salt cake. The reactions are the same as those shown in the laboratory preparation.

Niter cake, a by-product made in the manufacture of nitric acid, contains impure sodium bisulphate and about 32 per cent. of free sulphuric acid. This material is now being used instead of pure sulphuric acid to react with sodium chloride to form hydrogen chloride. This is a good example of the application to a manufacturing process of a material that would otherwise be a waste product.

The niter cake and salt are crushed and mixed in proper proportion, which depends on conditions. The mixture is then fed into the top of a furnace, as shown in Fig. 3, the temperature of which is about 215° C. At this stage, the sulphuric acid in the niter cake reacts with the salt to produce hydrogen chloride. The residue, salt cake, is removed for use in the manufacture of glass, etc.

The hydrogen chloride rises to the top of the furnace and enters a series of stoneware **U** tubes and a water box where the gas is cooled. The hydrogen chloride next passes through a quartz filter, where its impurities are removed. It next enters a series of absorption arrangements, called tourilles, containing dilute hydrochloric acid, where the gas forms a strong solution with water. Gas that is not dissolved at this point passes up through absorption towers filled with coke for retarding the passage of the gas so that the maximum amount will be absorbed by water passing down through the towers. The solution of acid flowing back from the towers passes back into the absorption

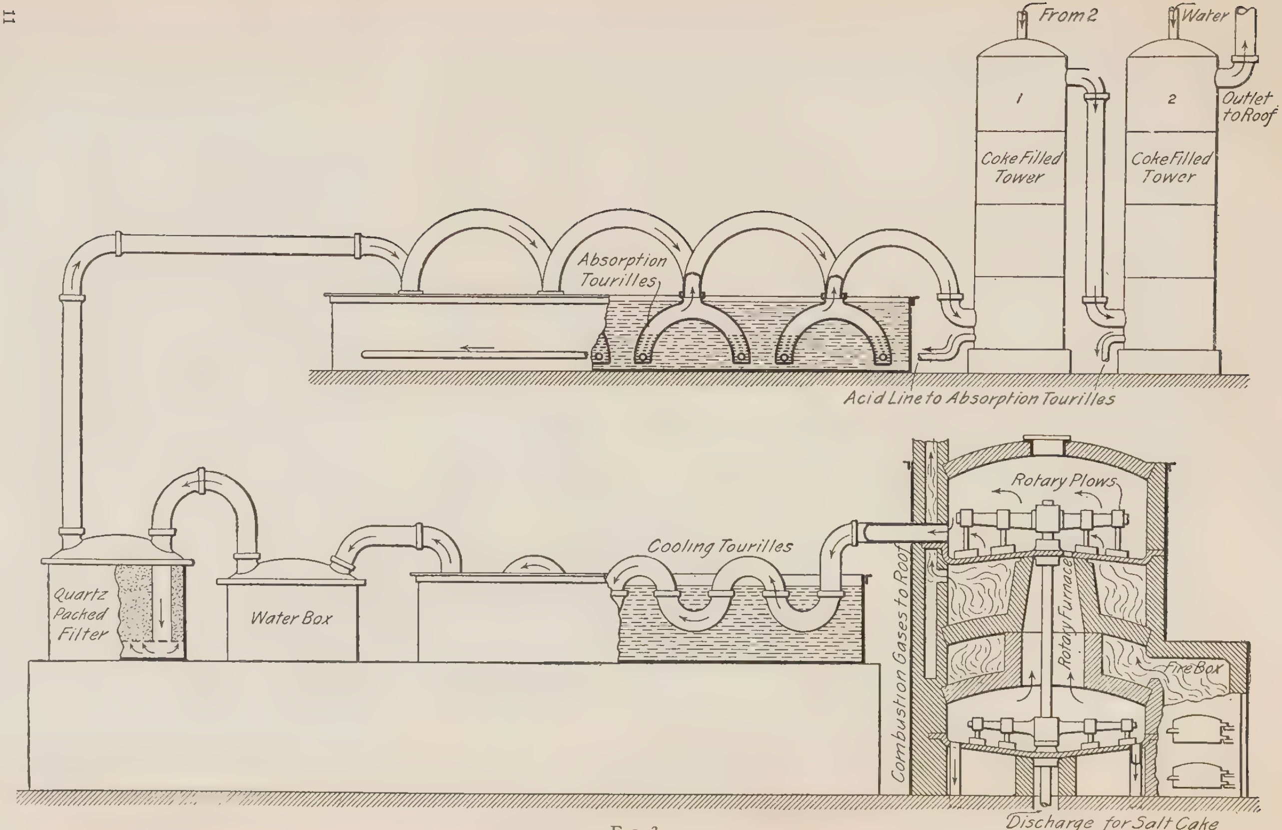

From 2
Water
1
2
Outlet to Roof
Coke Filled Tower
Coke Filled Tower
Absorption Tourilles
Acid Line to Absorption Tourilles
Rotary Plows
Cooling Tourilles
Quartz Packed Filter
Water Box
Combustion Gases to Roof
Rotary Furnace
Fire Box
Discharge for Salt Cake

FIG. 3

tourilles, where it absorbs more hydrogen chloride to form concentrated hydrochloric acid.

15. Physical Properties.—Hydrogen chloride is a colorless, pungent, acid gas; it fumes strongly in the air, is unfit for breathing, and extinguishes flame. It is about one-fourth heavier than air, having a specific gravity of 1.269, and is extremely soluble in water. Under ordinary conditions of temperature and pressure, 1 volume of water dissolves nearly 500 volumes of the gas. If such a solution is heated, the gas passes off until at boiling point, 110° C., but 20.2 per cent. by weight of hydrogen chloride is left in the solution. Continued boiling does not alter the percentage of gas in solution.

Hydrogen chloride fumes brought in contact with moist air form a solution of hydrogen chloride. It neither burns nor supports combustion. The critical temperature of hydrogen chloride is 51.4° C., and its critical pressure is 81.5 atmospheres. Pure, liquid HCl boils at $-83.1°$ C.; the liquid may be frozen to a solid, which melts at $-112.5°$ C.

The muriatic, or hydrochloric acid of commerce is simply a solution of the gas in water, and may be recognized by its fumes and the peculiar odor given out when exposed to the air. It is usually yellow because of the iron in solution. The ordinary pure concentrated or fuming hydrochloric acid of commerce usually has a specific gravity of 1.20 and contains 39 per cent. HCl.

16. Chemical Properties.—Hydrogen chloride is chemically rather inert and stable. This gas has no action on non-metals such as carbon and sulphur, but it does react with some of the more active metals such as potassium, sodium, and magnesium, to form chlorides of these metals with the liberation of hydrogen. It combines directly with ammonia gas, NH_3, to form a dense cloud of ammonium chloride, NH_4Cl.

Hydrochloric acid, the solution of hydrogen chloride in water, exhibits marked chemical properties. It is a strong acid, turning blue litmus red, reacting with metals to liberate hydrogen and to form chlorides of the respective metals, and

with oxides and hydroxides of metals to form chlorides of the metals and water. Following are some chemical equations showing these changes:

With metals, hydrochloric acid forms:

$$Zn + 2HCl = ZnCl_2 + H_2$$
$$Fe + 2HCl = FeCl_2 + H_2$$
$$2Na + 2HCl = 2NaCl + H_2$$

With bases, hydrochloric acid forms:

$$KOH + HCl = KCl + H_2O$$
$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$$

TABLE I

ORDER OF ACTIVITY OF METALS

(Most Active)
Potassium
Sodium
Calcium
Magnesium
Aluminum
Chromium
Manganese
Zinc
Cadmium
Iron
Nickel
Tin
Lead
Hydrogen
Antimony
Copper
Mercury
Silver
Platinum
Gold
(Least Active)

All the metals above hydrogen in Table I can replace hydrogen in hydrochloric and other acids. The ease with which these reactions take place increases with the metals as they progress from lead to potassium. For instance, metallic potassium reacts much more vigorously with hydrochloric acid than does zinc, iron, or tin; manganese reacts more vigorously than zinc, tin, or lead; and so on. In like manner, the metals listed below hydrogen, such as copper, mercury, and gold, do not replace hydrogen in hydrochloric acid.

17. Chlorides.—Most chlorides are soluble in water. The common exceptions are: Mercurous chloride, $HgCl$; silver chloride, $AgCl$; and lead chloride, $PbCl_2$. Less common exceptions are: Cuprous chloride, $CuCl$; aurous chloride, $AuCl$; and thallous chloride, $TlCl$. This fact is the basis for many manipulations and tests made by the analytical chemist.

18. Uses for Hydrochloric Acid.—Hydrochloric acid has a wide range of industrial uses and is lending itself yearly to new ones. One of its chief applications is in the process of removing scale and rust from a metal to cleanse it before coating it with tin. This cleansing process is called pickling. It is also used in the manufacture of bleaches, glue, and gelatine, and in the

reduction of tungsten ores. Its uses in the laboratory are varied and numerous.

19. Composition.—The composition of hydrochloric acid may also be shown by the electrolysis of the aqueous solution.

TABLE II

SPECIFIC GRAVITY OF HYDROCHLORIC ACID

$\frac{15^\circ}{4^\circ}$ C.

Specific Gravity	Degrees Baumé	Per Cent. *HCl*	Specific Gravity	Degrees Baumé	Per Cent. *HCl*
1.000	0.0	0.16	1.105	13.6	20.97
1.005	0.7	1.15	1.110	14.2	21.92
1.010	1.4	2.14	1.115	14.9	22.86
1.015	2.1	3.12	1.120	15.4	23.82
1.020	2.7	4.13	1.125	16.0	24.78
1.025	3.4	5.15	1.130	16.5	25.75
1.030	4.1	6.15	1.135	17.1	26.70
1.035	4.7	7.15	1.140	17.7	27.66
1.040	5.4	8.16	1.145	18.3	28.61
1.045	6.0	9.16	1.150	18.8	29.57
1.050	6.7	10.17	1.155	19.3	30.55
1.055	7.4	11.18	1.160	19.8	31.52
1.060	8.0	12.19	1.165	20.3	32.49
1.065	8.7	13.19	1.170	20.9	33.46
1.070	9.4	14.17	1.175	21.4	34.42
1.075	10.0	15.16	1.180	22.0	35.39
1.080	10.6	16.15	1.185	22.5	36.31
1.085	11.2	17.13	1.190	23.0	37.23
1.090	11.9	18.11	1.195	23.5	38.16
1.095	12.4	19.06	1.200	24.0	39.11
1.100	13.0	20.01			

The apparatus used for this purpose is known as Hofmann's apparatus for the decomposition of hydrochloric acid, and is shown in Fig. 4. It consists of three glass tubes connected at

the bottom. The bottoms of the two outer tubes are closed with rubber stoppers through which pass carbon electrodes *A* and *B*. Platinum electrodes can be used, but carbon is best, as nascent chlorine acts on platinum. The apparatus is filled to the level of the stop-cocks *C* and *D*, which are open, through the funnel *G*. A battery is connected with *A* and *B* through the wires *E* and *F*. After a time *C* and *D* are closed, when equal volumes of hydrogen and chlorine will collect in the tubes. The hydrogen will rise from the negative electrode and the chlorine from the positive. The chlorine gas can be recognized by its color and the hydrogen by its inflammability. The chlorine can be further recognized by its reddening a piece of blue litmus paper.

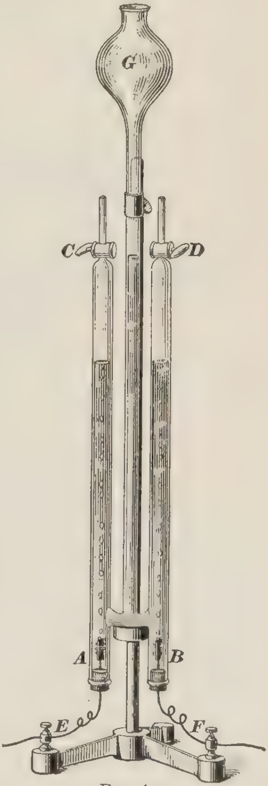


Fig. 4

20. Chlorine, like oxygen, is liberated from the electrode connected with the copper or platinum element of the battery. The following eight elements are similar in this respect, and from their behavior with an electric current are called negative: Oxygen, chlorine, bromine, iodine, fluorine, sulphur, selenium, and tellurium.

Another convenient apparatus is shown in Fig. 5. The **U**-tube *B* containing calcium chloride, for the purpose of drying the evolved gas, is fitted to the generating flask *A* which contains salt and sulphuric acid. The right-hand limb of the **U**-tube is connected to the two bulbs *C* and *D*, the first containing dry, finely pulverized manganese dioxide.

Arrange a glass jar *F* to receive the escaping gas; place in it a sheet *G* of moist blue litmus paper. The hydrochloric acid evolved at once changes the color of the litmus paper. Apply

heat to the bulb containing manganese dioxide; the hydrochloric acid is decomposed; water collects in the second bulb *D*,

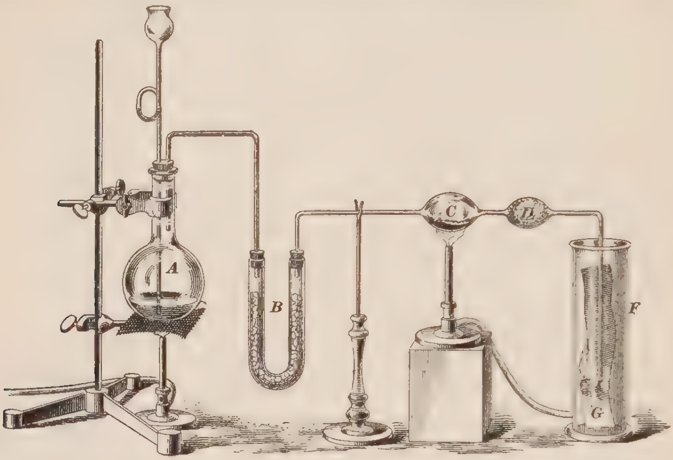


FIG. 5

and chlorine passes over into the jar *F*. It may be easily recognized by its odor and bleaching power.

OXIDES AND OXYACIDS

21. Oxides and Oxyacids of Chlorine.—In addition to hydrochloric acid, there are other acids containing chlorine, hydrogen, and oxygen, which vary in the amounts of oxygen present. Following is a list of the names and formulas of the substances:

OXIDES	ACIDS
Hypochlorous anhydride, Cl_2O	Hypochlorous, $HClO$
Chlorine dioxide, ClO_2	Chlorous, $HClO_2$
Perchloric anhydride, Cl_2O_7	Chloric, $HClO_3$
	Perchloric, $HClO_4$

POTASSIUM SALTS

Potassium hypochlorite, $KClO$
Potassium chlorite, $KClO_2$
Potassium chlorate, $KClO_3$
Potassium perchlorate, $KClO_4$

22. Nomenclature.—In connection with the preceding names and formulas, it should be noted that the suffixes *ic* and *ous* indicate more or less oxygen, respectively; the prefix *hypo* means still less and *per* still more oxygen. These suffixes and prefixes are relative terms used within this particular group; their meanings will also be the same when used for other acid groups, such as H_2SO_4 and H_3PO_4, so far as they apply to the oxygen contents of the different acids which make up the group.

HYPOCHLOROUS ANHYDRIDE, OR CHLORINE MONOXIDE

Formula Cl_2O. *Molecular weight 86.92*

23. Preparation.—Hypochlorous anhydride, or chlorine monoxide, is a gas that was discovered by Balard in 1834. It is formed when dry chlorine is passed over mercuric oxide:

$$2HgO + 2Cl_2 = Cl_2O + Hg_2OCl_2$$

In order to obtain satisfactory results, the mercuric oxide used is prepared by precipitation from mercuric nitrate solution by sodium hydroxide, thus:

$$Hg\,(NO_3)_2 + 2NaOH = HgO + 2NaNO_3 + H_2O$$

The precipitate is thoroughly washed on the filter with water, dried, and then heated to about 400° C.; after cooling, it may be used.

The chlorine monoxide obtained is condensed in a bent glass tube, part of which is immersed in ice water or a freezing mixture. The gas, which is of a brownish-yellow color, has a specific gravity of 2.977 and is easily condensed to a reddish-brown liquid boiling at 5° C. In the gaseous condition it has a penetrating odor somewhat resembling that of chlorine, and attacks the respiratory organs very energetically. It is very unstable, decomposing explosively if heated even by the hands or when exposed to the action of the electric spark, into two volumes of chlorine and one volume of oxygen.

$$2Cl_2O = 2Cl_2 + O_2$$

It is also decomposed with violence when brought into contact with sulphur, phosphorus, or an organic substance such as

rubber. It has strong bleaching properties. Hydrochloric acid decomposes it into water and free chlorine. It is quite soluble in water, the latter dissolving 200 volumes of the gas at 0° C., forming hypochlorous acid:

$$Cl_2O+H_2O=2HClO$$

HYPOCHLOROUS ACID

Formula HClO. Molecular weight 52.468

24. Preparation and Properties.—Hypochlorous acid, $HClO$, is known only in its aqueous solution. It is prepared by passing chlorine monoxide into water or by passing chlorine into water containing freshly precipitated mercuric oxide in suspension. The liquid must be agitated continually and kept in the dark.

$$HgO+2Cl_2+H_2O=HgCl_2+2HClO$$

It has a peculiar odor suggesting chlorine and is a powerful oxidizing and bleaching agent owing to the ease with which it decomposes into hydrochloric acid and oxygen. Hydrochloric acid decomposes hypochlorous acid into chlorine and water with the evolution of twice the quantity of chlorine present in the hypochlorous acid:

$$HClO+HCl=Cl_2+H_2O$$

25. Commercial Manufacture of Hypochlorites. Commercially, neither hypochlorous acid nor its pure salts are made, for the impure hypochlorites can be manufactured more cheaply and serve just as well in industrial operations.

Chlorine unites with the hydroxide of sodium, potassium, or calcium in the presence of moisture to form the corresponding hypochlorite, as shown in these reactions:

$$2NaOH+Cl_2=NaClO+NaCl+H_2O$$
$$2KOH+Cl_2=KClO+KCl+H_2O$$
$$2Ca\,(OH)_2+2Cl_2=Ca(OCl)_2+CaCl_2+2H_2O$$

The chlorides present with the hypochlorites do not interfere with the action of the latter and no effort is, therefore, made to separate them. Solutions of sodium hypochlorite mixed

with a little sodium chloride present as an impurity, and aqueous solutions of a mixture of potassium hypochlorite and potassium chloride are commonly known as Labarraque's and Javel solutions, respectively.

Aqueous solutions of hypochlorites are produced in large quantities for immediate use at the place of manufacture, but, owing to the bulk of the hypochlorite solutions and their instability, they are not generally transported.

The hypochlorites of sodium or potassium can be made by treating calcium hypochlorite with the carbonate of sodium or potassium, respectively, as shown in these reactions:

$$Ca\ (ClO)_2 + Na_2CO_3 = 2NaClO + CaCO_3$$
$$Ca\ (ClO)_2 + K_2CO_3 = 2KClO + CaCO_3$$

26. Manufacture of Bleaching Powder.—In practical work calcium hypochlorite is used for bleaching and other purposes as it is cheaper than either sodium hypochlorite or potassium hypochlorite, and meets the same requirements of both of these salts for many purposes. It is manufactured in large quantities by absorbing chlorine in a suspension of hydrated lime, $Ca\ (OH)_2$, in water, called milk of lime. In this process, the temperature must be kept below 35° C. and an excess of lime must always be present, or the hypochlorite will begin to decompose with the formation of calcium chlorate. In the manufacture of this solution of calcium hypochlorite, also called bleach liquor, the chlorine gas is generally mixed with air before it is passed into the suspension of lime so as to prevent overheating.

27. In another process for the manufacture of bleaching powder, burnt lime that is low in magnesium oxide and free from carbon dioxide, is spread in a layer about 3 inches deep in a chamber having a floor of asphalt and sides of lead, stone, or cement. This chamber is connected to a series of similar chambers, the floors of which are also covered with lime. A mixture containing about 40 per cent. of chlorine and 60 per cent. of air, is admitted through the roof of the first chamber. It passes slowly over the lime in this chamber and is partially absorbed, then passes into the second chamber, where

it is further absorbed, and so on until it is practically all absorbed. As soon as the lime has absorbed all the chlorine it can, it is placed either in wooden casks or in iron drums for shipment.

Bleaching powder, known also as chloride of lime, is the most convenient and economical kind of bleaching material as far as portability is concerned. It is a white, porous powder with an odor of chlorine. It has a strong alkaline reaction, and is a strong bleaching agent. It decomposes in the air, and is soluble in water, although the commercial product always leaves a residue of calcium hydroxide. Bleaching powder alone does not act very rapidly as a bleaching agent. Carbon dioxide blown through the solution or the addition of dilute acids hastens the action. It is also used as a disinfectant and as an antiseptic.

28. Composition of Bleaching Powder.—The formula commonly assigned to bleaching powder is $Ca(OCl)_2 \cdot CaCl_2$. Its constitution as thus represented has been the subject of much discussion, however, and the matter has not yet been definitely settled.

One objection to the view that calcium chloride is present in bleaching powder is the fact that the substance is not deliquescent, as it should be if calcium chloride were present. Again, practically all of the chlorine present in bleaching powder can be expelled by carbon dioxide, which would not be the case if $CaCl_2$ were present. This has led to the suggestion that it is a compound of the formula $CaOCl_2$.

On the other hand, dilute hydrochloric or sulphuric acid decomposes it, liberating double the quantity of chlorine found in the contained hypochlorite:

$$Ca(ClO)_2 + CaCl_2 + 2H_2SO_4 = 2CaSO_4 + 2Cl_2 + 2H_2O$$

which would indicate that $CaCl_2$ or some other compound containing chlorine is present.

29. Chlorates.—Of the salts of chloric acid, the one called potassium chlorate is the best known and most abundantly used. It can be made by passing an excess of

chlorine into a hot (60° C. to 70° C.) concentrated solution of potassium hydroxide, as shown in this reaction:

$$3Cl_2+6KOH=KClO_3+5KCl+3H_2O$$

But as in this process 5 molecules of potassium chloride are made for each molecule of potassium chlorate, a more economical way of making potassium chlorate is used, based on the fact that calcium chloride is cheaper than potassium chloride.

In the latter process, calcium hydroxide, as milk of lime, instead of potassium hydroxide, serves as the raw material. Chlorine in excess is passed over milk of lime in cast-iron cylinders provided with stirrers, until most of the calcium hydroxide has been acted on by the gas. The chlorine that is not taken up by calcium hydroxide in the first cylinder passes on into a second one where more calcium hydroxide is acted on. In this change calcium chlorate and calcium chloride are formed as shown by the reaction:

$$6Ca(OH)_2+6Cl_2=Ca(ClO_3)_2+5CaCl_2+6H_2O$$

Potassium chloride is then added to the solution of calcium chloride and calcium chlorate, whereupon calcium chlorate is changed to potassium chlorate; thus:

$$Ca(ClO_3)_2+2KCl=2KClO_3+CaCl_2$$

Water is evaporated until the solution has a specific gravity of 1.35. When the solution is cooled, potassium chlorate crystals, being less soluble than those of calcium chloride, separate out. The liquor left after the potassium chlorate has been removed, called the *mother liquor*, is concentrated by evaporating off part of its water a second and possibly a third time, the solution being cooled after each evaporation, to recover the small amount of potassium chlorate left. The crude potassium chlorate is purified by redissolving it in water and by recrystallizing it again by concentrating and cooling.

30. As sodium chlorate is more readily soluble than potassium chlorate, the method of making it is somewhat different from that used in making the potassium salt. Calcium chlorate is made in the same way and sodium chloride is then added to the solution. The mixture is then boiled down until it is of a

specific gravity of 1.50 and cooled. About four-fifths of the calcium chloride (being less soluble than sodium chlorate) crystallizes from the solution. The remaining liquor is drained off and most of the calcium salt is precipitated as calcium sulphate by the addition of sodium sulphate, thus:

$$CaCl_2+Na_2SO_4=CaSO_4+2NaCl$$

The solution of sodium chloride and sodium chlorate is separated from the precipitate of calcium sulphate and is boiled down. Most of the sodium chloride separates from the boiling solution and is removed, and upon cooling the solution most of the sodium chlorate, which crystallizes, is recovered.

31. Fractional Crystallization.—The manufacture of potassium and sodium chlorates brings out a method of separating two soluble products. Both potassium chlorate and calcium chloride are soluble, but the former is less soluble than the latter. If the solution is concentrated, that is, if the amount of solvent present is reduced and the temperature of the solvent is lowered, less substance can remain in solution. A point is finally reached where the solvent cannot hold in solution all of the dissolved materials, and a part of it must separate from the solution. In such cases, the less soluble material separates first. The process whereby soluble substances are separated from one another by crystallizing the least soluble substance first, and then the others present in order of their solubilities, is known as fractional crystallization. It is the crystallization of a substance from a solution in fractions each of which is more soluble than the fraction previously removed.

32. Electrolytic Manufacture of Hypochlorites and Chlorates.—The electrolysis of an alkali chloride solution results in the production of the alkali metal and chlorine; thus:

$$NaCl=\overset{+}{Na}+\overset{-}{Cl}$$
$$2Na+2H_2O=2NaOH+H_2$$

If the electrolytic cell is so constructed that the chlorine and sodium hydroxide are brought into contact, a condition exists

that permits of the manufacture of either the chlorate or the hypochlorite of sodium, depending on the conditions; thus:

$$2NaOH + Cl_2 = NaClO + NaCl + H_2O$$

or

$$6NaOH + 3Cl_2 = NaClO_3 + 5NaCl + 3H_2O$$

Above 40° C. and with the solution slightly acid, the chlorate is made; below 40° C. and with the solution less acid, hypochlorite is produced. In practice, a temperature of 70° to 100° C. is maintained in the production of chlorate.

33. Uses of Chlorates.—Chlorates are the chief sources of oxygen in the laboratory and are extensively used in industrial work where a substance that yields oxygen readily is needed, as in fireworks, matches, and explosives.

CHLORIC ACID

Formula $HClO_3$. *Molecular weight 84.468*

34. Preparation and Properties.—Chloric acid, $HClO_3$, the most important of the chlorine oxyacids, is prepared by decomposing barium chlorate, in aqueous solution, by means of sulphuric acid:

$$\underset{\text{barium chlorate}}{Ba(ClO_3)_2} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{barium sulphate}}{BaSO_4} + \underset{\text{chloric acid}}{2HClO_3}$$

The clear solution of the chloric acid is poured off from the precipitated barium sulphate and carefully evaporated in vacuum over strong sulphuric acid. This then contains 40 per cent. of pure chloric acid and corresponds to the formula $HClO_3 \cdot 7H_2O$. Attempts to concentrate a solution of chloric acid beyond this point have caused the acid to break down with a rapid evolution of chlorine and oxygen gas and the formation of perchloric acid.

35. By adding fluosilicic acid to a solution of potassium chlorate, the latter is decomposed and the potassium precipitated as insoluble fluosilicate, while chloric acid is found in the solution:

$$\underset{\substack{\text{potassium}\\\text{chlorate}}}{2KClO_3} + \underset{\substack{\text{fluosilicic}\\\text{acid}}}{H_2SiF_6} = \underset{\substack{\text{chloric}\\\text{acid}}}{2HClO_3} + \underset{\substack{\text{potassium}\\\text{fluosilicate}}}{K_2SiF_6}$$

On evaporating the solution at a temperature not exceeding 38° C., the chloric acid is obtained as a slightly yellow, sirupy liquid with a pungent odor. This solution has a specific gravity of about 1.28, and contains about 40 per cent. of $HClO_3$. It does not change rapidly at ordinary temperatures, but above 40° C. it is decomposed by continued exposure to light according to the equation:

$$3HClO_3 = HClO_4 + H_2O + Cl_2 + 2O_2$$

It is a very powerful oxidizing agent. Organic substances such as wood and paper decompose the acid at once, and are themselves oxidized so rapidly as to take fire. An aqueous solution of chloric acid is colorless, has a pungent smell, a powerful acid reaction, and bleaches vegetable colors quickly. It is a monobasic acid. Its salts, the chlorates, are also very active oxidizing agents.

36. All the chlorates are soluble in water but not to as great an extent as the chlorides. Reducing agents (nascent hydrogen, sulphur dioxide) convert them into the corresponding chloride. Chlorates are distinguished from chlorides by the fact that they give no precipitate with silver nitrate. If the chlorate is heated, however, the oxygen is driven off, and the chloride is formed, and this will produce a white precipitate with silver nitrate.

CHLORINE DIOXIDE

Formula ClO_2. *Molecular weight 67.46*

37. Preparation and Properties.—Chlorine dioxide, or chlorine peroxide as it is also called, is always formed along with perchloric acid, when sulphuric acid acts on potassium chlorate, and results from the decomposition of chloric acid which is first formed, as shown by the equations:

$$2KClO_3 + H_2SO_4 = K_2SO_4 + 2HClO_3;$$
$$3HClO_3 = HClO_4 + H_2O + 2ClO_2$$

It is an extremely unstable reddish-yellow gas, which can be condensed to a dark-red liquid that boils at 9° C. and freezes at −79° C. to an orange-colored crystalline mass. The gaseous

and liquid dioxide are subject to sudden violent decomposition, although the liquid dioxide may be distilled without decomposition if no trace of organic matter is present.

Chlorine dioxide is much heavier than air, having a specific gravity of 2.315, and must be collected by upward displacement of air, as it is decomposed by mercury and is soluble in water. It possesses a peculiar odor like that of chlorine and burnt sugar.

Combustible substances such as phosphorus, ether, sugar, etc., take fire spontaneously when thrown into chlorine dioxide gas. At 4° C., water dissolves about twenty times its volume of chlorine dioxide and forms a bright yellow solution, which is decolorized by alkalies forming salts of chloric and chlorous acids:

$$2KOH+2ClO_2=KClO_3+KClO_2+H_2O$$

38. Chlorous Acid and Chlorites.—Although chlorous acid, $HClO_2$, has never been isolated, a number of its salts are known, among the most common and important being potassium chlorite, $KClO_2$, and silver chlorite, $AgClO_2$. Potassium chlorite is formed when a solution of potassium hydroxide is added to a solution of chlorine dioxide in water;

$$2KOH+2ClO_2=KClO_2+KClO_3+H_2O$$

Silver chlorite is obtained when an aqueous solution of silver nitrate is mixed with a solution of potassium chlorite:

$$AgNO_3+KClO_2=AgClO_2+KNO_3$$

The chlorites are all unstable compounds. The alkali chlorites are all soluble in water. If the lead salt, $Pb(ClO_2)_2$, is heated for a short time at 100° C., it decomposes with violence, and if rubbed in a mortar with sulphur or with some metallic sulphides, it ignites. The soluble chlorites have a caustic taste and bleach vegetable coloring matters. They are distinguished from the hypochlorites by the fact that the addition of arsenious acid does not destroy this bleaching power.

PERCHLORIC ACID

Formula $HClO_4$. Molecular weight 100.468

39. Preparation and Properties.—Perchloric acid is formed when chloric acid is decomposed by means of heat or light:

$$3HClO_3 = HClO_4 + Cl_2 + 2O_2 + H_2O$$

It is more conveniently obtained, however, from its salts, the perchlorates. When heated to fusion, potassum chlorate at first breaks up according to the equation:

$$2KClO_3 = KClO_4 + KCl + O_2$$

If the heat is removed, no further decomposition takes place and the perchlorate can be separated from the chloride by treating the mixture with cold water in which the chloride dissolves readily, while the perchlorate is but slightly soluble. From the perchlorate thus obtained, perchloric acid may be prepared by distilling it with sulphuric acid, perchloric acid being set free, thus:

$$2KClO_4 + H_2SO_4 = K_2SO_4 + 2HClO_4$$

Perchloric acid is the most stable of the oxyacids of chlorine. It is a heavy, colorless, fuming liquid, having a specific gravity of 1.764 at 22° C., which boils at 39° C., under a pressure of 56 millimeters. It is a dangerous substance to handle, as it produces bad flesh wounds when brought in contact with the skin, and if brought in contact with organic matter or charcoal, it decomposes with explosive violence. It dissolves in water with a hissing sound, forming the hydrate, $HClO_4 \cdot H_2O$, while some facts point to the existence of a second hydrate, $HClO_4 \cdot 2H_2O$. A 70 per cent. solution of perchloric acid is perfectly stable and may be kept indefinitely.

40. Perchloric Anhydride, or Chlorine Heptoxide. This compound is formed when perchloric acid is digested with phosphorus pentoxide, P_2O_5, at temperatures below $-10°$ C. The reaction which occurs may be represented as follows:

$$P_2O_5 + 2HClO_4 = 2HPO_3 + Cl_2O_7$$

The perchloric anhydride is separated from the metaphosphoric acid, which is also formed, by distillation.

Perchloric anhydride is a colorless liquid which explodes when struck or strongly heated. It boils at 82° C. under normal pressure.

41. Anhydrides.—Hypochlorous anhydride and perchloric anhydride are called anhydrides because they form hypochlorous acid and perchloric acid, respectively, when combined with water, thus:

$$Cl_2O+H_2O=2HClO$$
$$Cl_2O_7+H_2O=2HClO_4$$

As previously stated the term anhydride is applied to oxides that form acids when combined with water. The number of molecules of water combining with 1 of the oxide will vary with different compounds. The name of the anhydride is taken from the acid formed. For example, SO_3 is called, not only sulphur trioxide, but also sulphuric anhydride, because, combined with water, it forms sulphuric acid as shown in the equation:

$$SO_3+H_2O=H_2SO_4$$

Likewise, N_2O_5, nitrogen pentoxide, is also called nitric anhydride, because it combines with water to form nitric acid, thus:

$$N_2O_5+H_2O=2HNO_3$$

BROMINE

OCCURRENCE, PREPARATION, AND PROPERTIES

Symbol Br. Atomic weight 79.92. Molecular formula Br_2. Molecular weight 159.84.

42. History.—Bromine was discovered by Balard in 1826 in the examination of bittern, which is the liquid remaining after the sodium chloride and some other salts have been made to crystallize by evaporating sea-water, which contains only about 1 grain of bromine per gallon in the forms of bromide of magnesium and bromide of sodium. Owing to its disagreeable

odor, he gave it the name bromine, which is derived from the Greek word *bromos*, stench.

43. Occurrence.—Like chlorine, this element is never found uncombined in nature but always in combination with other elements such as sodium, potassium, and magnesium. It occurs in the waters of the springs of Kreuznach and Kissingen in Germany and also has been obtained from various saline springs in the United States (Ohio, Michigan, Kentucky, and Pennsylvania), and from the mother liquors of the salt works at Stassfurt, in Germany.

44. Preparation.—The first step in the preparation of bromine, by any process, is to separate the bromides from the chlorides with which they are associated. The solid salts are dissolved, or, if already in solution, are concentrated by evaporation; the chlorides, being less soluble, first crystallize out and leave a mother liquor, or bittern, in which the bromides predominate. From this point on, the methods for recovering the bromine differ slightly as to details.

45. In the laboratory or on a small scale where a very pure product is desired, chlorine is passed through the bittern or concentrated solution of the bromides and bromine is liberated as represented by the following equation:

$$\underset{\substack{\text{magnesium}\\\text{bromide}}}{MgBr_2} + \underset{\text{chlorine}}{Cl_2} = \underset{\substack{\text{magnesium}\\\text{chloride}}}{MgCl_2} + \underset{\text{bromine}}{Br_2}$$

The bromine at first set free imparts a reddish-brown color to the solution. On shaking this with ether the bromine is dissolved, and its ethereal solution rises to the surface, and may be poured from the watery layer underneath. Upon treating the ethereal solution with potassium hydroxide, its red color disappears, bromide and bromate of potassium being formed:

$$\underset{\text{bromine}}{3Br_2} + \underset{\substack{\text{potassium}\\\text{hydroxide}}}{6KOH} = \underset{\substack{\text{potassium}\\\text{bromide}}}{5KBr} + \underset{\substack{\text{potassium}\\\text{bromate}}}{KBrO_3} + \underset{\text{water}}{3H_2O}$$

46. The ether is then distilled off and collected; the solid residue of bromide and bromate is ignited in order to decom-

pose the bromate, which splits up into bromide and oxygen in the same manner as does potassium chlorate. In this way potassium bromide is obtained; the bromine may again be liberated by gently heating the bromide with manganese dioxide and sulphuric acid, when a reaction occurs analogous to that which takes place when a chloride is similarly heated:

$$\underset{\text{potassium bromide}}{2KBr} + \underset{\text{sulphuric acid}}{3H_2SO_4} + \underset{\text{manganese dioxide}}{MnO_2}$$
$$= \underset{\text{acid potassium sulphate}}{2KHSO_4} + \underset{\text{manganese sulphate}}{MnSO_4} + \underset{\text{bromine}}{Br_2} + \underset{\text{water}}{2H_2O}$$

47. In another process the mother liquor, instead of being treated with chlorine, is evaporated to dryness and the residue mixed directly with sulphuric acid and manganese dioxide; but in this case, as chlorides are always present in greater or less quantity, the bromine is very apt to be contaminated with chlorine.

One of the largest manufacturers of bromine in the United States has developed the following commercial process for the recovery of bromine from bittern. The reactions involved are those just given, the process differing only in some of its mechanical features.

The solution of bromides flows down through a tower, which is packed with stoneware balls or small pieces of stoneware of regular shape. As the solution trickles down from the top of the tower over the stoneware packing, it is spread out by the packing, thus offering a large surface, and is met by a regulated current of chlorine which enters at the bottom of the tower. Practically all of the chlorine is used up and the liberated bromine is led to the condensers. The solution, which now contains chlorides and some dissolved bromine, is treated with live steam. The bromine is expelled and led to the condenser.

48. Purification.—Crude bromine manufactured by any process may contain chlorine and iodine. The former may be removed by distilling the mixture with calcium bromide, $CaBr_2$, or ferrous bromide, $FeBr_2$:

$$2FeBr_2 + 3Cl_2 = 2FeCl_3 + 2Br_2$$

Iodine may be removed by treating the mixture with a copper salt, cuprous iodide being precipitated:

$$I_2+2CuBr_2=2CuI+2Br_2$$

Dry, or anhydrous, bromine may be produced by distilling bromine in the presence of concentrated sulphuric acid.

49. Properties.—Bromine, at ordinary temperatures, is a dark, brownish-red liquid, so heavy (sp. gr. 3.1883 at 0° C.) that glass floats readily in it; it possesses an exceedingly penetrating and disagreeable odor, somewhat recalling that of chlorine. At a temperature of 58.7° C., it boils and is converted into a deep-red vapor that is about five and one-half times more dense than air. Bromine freezes at −7.2° C., forming a dark-brown mass of delicate needles, with a metallic luster. Water dissolves bromine but slightly, 33 parts of it dissolving at a temperature of 15° C. only 1 part of bromine. It is readily soluble, however, in carbon bisulphide, chloroform, alcohol, and ether. This solution possesses bleaching powers, but not to the same extent as chlorine. In this, as in other reactions, bromine and chlorine closely resemble each other, but bromine is the less active of the two and is displaced from its compounds by chlorine. It is an active corrosive poison.

Bromine colors starch yellow, and a bromide in aqueous solution precipitates silver from its solutions as yellow silver bromide.

$$AgNO_3+NaBr=AgBr+NaNO_3$$

Bromine and its salts are used principally in photography and in medicine.

IODINE

OCCURRENCE, PREPARATION, AND PROPERTIES

Symbol I. Atomic weight 126.92. Molecular formula I_2. *Molecular weight 253.84.*

50. History and Occurrence.—Iodine, as well as bromine and chlorine, is found in sea-water, but in much smaller quantities. Sodium iodide, *NaI*, appears to constitute

a portion of the necessary food of certain varieties of seaweed, which extract it from the sea-water and concentrate it in their tissues. On the coasts of Scotland and Normandy large masses of seaweed were formerly burned in order to extract the sodium salts that they contained. The ash remaining, called kelp, or varec, was dissolved in water, and the sodium salts crystallized out. In the year 1811, Curtois, a soap manufacturer of Paris, being engaged in the manufacture of sodium salts from kelp, obtained from the waste liquors a substance that possessed properties different from those of any matter with which he was acquainted. He turned this substance over to Clement, a French chemist, who satisfied himself that it was an entirely new and hitherto unknown substance. Davy and Gay-Lussac in 1813 determined the elementary character of this substance, and named it iodine, derived from a Greek word in allusion to the beautiful violet color of its vapor.

51. Preparation.—Iodine is prepared from its salts in the same manner as is chlorine and bromine, by the treatment of the iodides with manganese dioxide and sulphuric acid:

$$2KI+MnO_2+2H_2SO_4=K_2SO_4+MnSO_4+2H_2O+I_2$$

Upon heating the mixture thus obtained, the iodine vapor passes over and is condensed.

Iodine is obtained on a large scale from seaweed. On the coasts of Scotland, Ireland, and France the gathering and burning of the seaweed affords occupation for many of the inhabitants. The seaweed is spread out to dry, after which it is burned to remove the organic matter. The mineral portions remaining as the ash is known as kelp, which contains from .1 to .5 per cent. of iodine. On lixiviating or digesting the kelp with water, a concentrated solution of the alkali chlorides, bromides, iodides, carbonates, sulphates, etc. is obtained. The chlorides, sulphates, and carbonates are allowed to crystallize, sulphuric acid is then added in order to decompose any hyposulphites or sulphides which may be present, and the sulphates formed are again separated by crystallization. The remaining liquor is then treated in several ways to obtain the iodine.

1. The liquors are distilled with a mixture of sulphuric acid and manganese dioxide in iron boilers heated to 60° C. and fitted with lead hoods. Each boiler is fitted with a lead pipe, which is connected in turn with a series of glass or earthware condensers, termed udells, fitting into each other. The iodine thus obtained is then further purified by resublimation, but even then it contains traces of the chloride and bromide.

2. In France the iodine is obtained by passing chlorine through the solution containing the iodide, when the iodine separates:

$$2KI + Cl_2 = 2KCl + I_2$$

If an insufficient quantity of chlorine is used, all the iodine is not obtained; whereas, if too much chlorine is used, the chloride of iodine, ICl_3, is obtained.

In later years the largest amount of iodine is obtained from the mother liquors of crude Chile saltpeter, $NaNO_3$. These liquors, which contain the iodine in the form of sodium iodate, are treated with sodium bisulphite, which reduces the sodium iodate to free iodine:

$$2NaIO_3 + 5NaHSO_3 = 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2$$

The iodine separates out in a solid form, is filtered off, and purified by sublimation. The commercial product thus obtained is washed with a little water, dried on porous plates, and resublimed.

52. Properties.—The properties of iodine are well marked; at ordinary temperatures it is a dark-colored (bluish-black) crystalline solid, possesses a metallic luster, and gives off small quantities of vapor of a violet tint. It melts at 115° C. and boils at 184.35° C., evolving a dense, violet, apparently black vapor that is 8.72 times heavier than air, and is the heaviest vapor known; at 1,700° C., however, the density of this vapor is reduced about one-half. The vapor possesses an odor resembling that of chlorine, which may even be noticed on smelling the substance at ordinary temperatures. Iodine is only very slightly soluble in water, to which it imparts a light yellowish-brown tint, 1 part of iodine requiring about 7,000 parts of water. It dissolves in carbon disulphide and chloro-

form, to which it imparts a violet tint, resembling the color of its vapor; it also dissolves in alcohol and ether, the two last-named substances forming with this element a brown solution. In chemical reaction iodine closely resembles chlorine and bromine, though it is less active than these two elements. It bleaches but faintly, if at all, in full sunlight, but combines directly with all metals to form iodides. Being less active than chlorine and bromine, it may be liberated from the iodides by the addition of either chlorine or bromine. On the other hand, the oxygen compounds of iodine are far more stable than those of chlorine and bromine.

Starch is the characteristic reagent for free iodine. It forms with it a deep-blue color, which is so intense that 1 part of iodine may be detected by it in 300,000 parts of water; this blue color vanishes on boiling, but reappears as the liquid cools. Iodine does not give this reaction when in a state of combination. The most delicate test for iodine is the purple-red color it produces when dissolved in carbon disulphide, CS_2; 1 part of iodine in 1,000,000 parts of water may be detected in this way. Iodine stains the skin yellow, but is not an active poison.

53. Uses.—Iodine, both free and in combination, has found an extended use in the manufacture of aniline colors and in medicine, being particularly serviceable in glandular affections. Iodine salts are also used extensively in photography.

FLUORINE

OCCURRENCE, PREPARATION, AND PROPERTIES

Symbol F. Atomic weight 19.0 Molecular formula F_2. Molecular weight 38.0.

54. Occurrence.—Fluorine occurs widely distributed in nature, but always in combination with other elements. It is found most frequently crystallized in cubes and octahedra, as the fluoride of calcium, CaF_2, under the name of fluorspar. It also occurs as cryolite, a fluoride of aluminum and sodium,

$3NaF+AlF_3$. It has also been detected in minute quantities in sea-water and in the water of many mineral springs. Fluorine has also been found in the enamel of the teeth, the bones of mammals, in the blood, the brains, and in milk. It is used in the form of fluorspar (from *fluo*, I flow) as a flux and derives its name from the property of melting that this compound has when heated. Owing to its remarkable affinity for other elements, fluorine has until recently resisted all attempts to isolate it.

55. Preparation.—Because of its great chemical activity, fluorine cannot be prepared in a manner similar to that in which the other halogens are obtained; it must therefore be prepared by a special method.

Hydrofluoric acid, *HF*, is first prepared by the action of sulphuric acid on fluorspar:

$$CaF_2+H_2SO_4=2HF+CaSO_4$$

After this acid has been carefully purified, it is thoroughly dried and strongly chilled. Sodium fluoride, *NaF*, is then added to the acid to make it a conductor of electricity and it is then subjected to the action of the current in a **U**-tube of platinum down the limbs of which the electrodes are inserted; the negative electrode is of platinum, while the positive one is made of an alloy of platinum and 10 per cent. of iridium. The **U**-tube is provided with stoppers of fluorspar and platinum delivery tubes for the gases, and is cooled to −23° C. The gaseous fluorine evolved at the positive electrode may be freed from hydrofluoric acid, *HF*, by the passage over dry potassium fluoride, *KF*, potassium hydrogen fluoride, KHF_2 being formed:

$$F_2+HF+KF=F_2+KHF_2$$

56. Properties.—Pure fluorine is a yellow-colored gas which may be condensed to a liquid, which boils at −187° C., and which may be frozen to a solid melting at −233° C. The element possesses an odor somewhat like that of hypochlorous acid. It possesses all of the chemical properties of chlorine much more strongly developed. Of all the known elements, fluorine is probably the most active. It unites directly with hydrogen even without the aid of light, and

decomposes water readily. Sulphur, selenium, phosphorus, iodine, arsenic, antimony, silicon, boron, potassium, and sodium take fire in it spontaneously. Potassium chloride and potassium iodide are readily decomposed by fluorine, which liberates the chlorine and iodine. Organic substances are violently attacked and inflamed in it. In the liquid form it loses its chemical properties almost completely. It unites readily, however, with hydrogen, but does not attack glass, iodine, sulphur, or metals. Oxides of the element are unknown. When fluorine is allowed to act on a small quantity of water, the latter is immediately decomposed, ozone and hydrofluoric acid being formed:

$$3F_2+3H_2O=6HF+O_3$$

Fluorine displaces chlorine from its compounds with the same ease that the latter displaces bromine and iodine from their compounds.

HYDROGEN COMPOUNDS OF BROMINE, IODINE, AND FLUORINE

57. Introductory.—The compounds of the halogens with hydrogen are known as hydrogen chloride, hydrogen bromide, hydrogen iodide, and hydrogen fluoride. These compounds, with the exception of hydrogen fluoride, are gases. The solutions which these compounds form with water have been designated as acids. Thus, hydrogen chloride is a gas, and hydrochloric acid is the gas dissolved in water.

58. Hydrogen Bromide.—Hydrogen bromide, HBr, is most conveniently prepared by the action of phosphorus on bromine, phosphorus tribromide being formed:

$$P_4+6Br_2=4PBr_3$$

The phosphorus tribromide, which is a colorless liquid, is then brought in contact with water, which easily decomposes it, hydrogen bromide and phosphorous acid being formed:

$$PBr_3+3H_2O=H_3PO_3+3HBr$$

The reactions described may be conveniently carried out in the laboratory according to the following directions:

About 5 grams of red phosphorus are mixed with about 40 to 50 grams of fine dry sand (to prevent subsequent packing of the phosphorus), and placed in the flask *A*, Fig. 6. To the contents of the flask is then added about 10 grams of water. About 15 grams of bromine are placed in the funnel *B* and covered with a cover glass. The bromine is allowed to drop gradually into the flask *A* by opening the stop-cock *C* slightly. The gas is passed through the **U**-tube *D* containing red phosphorus in order to free it of bromine, which might be carried over. The hydrobromic-acid gas is collected by upward

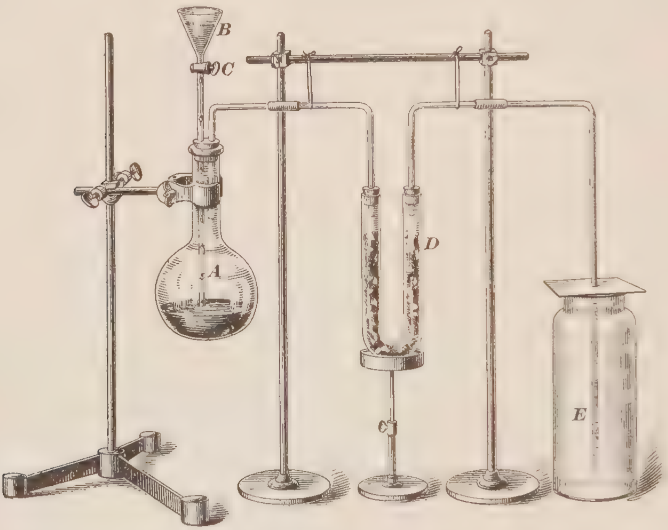


Fig. 6

displacement in the bottle *E*. A gentle heat may be applied to the flask *A* toward the end of the reaction. This work should be carried out under a hood or in a well-ventilated room.

Hydrogen bromide can be prepared also by the direct union of hydrogen and bromine vapors. The vapors are passed through a tube containing a platinum spiral heated to redness. As long as the hydrogen is in excess the hydrogen bromide is free from bromine.

It may also be formed by the action of sulphuric acid on a bromide, but, as it is not as stable as hydrogen chloride, it is

partly broken up by the sulphuric acid, and consequently cannot easily be obtained pure in this way.

59. Properties.—Hydrogen bromide is very similar to hydrogen chloride; it is a colorless acid gas, fuming strongly in moist air, and is very soluble in water. It may be condensed to a liquid which boils at −68.7° C., and when frozen to a solid it melts at −86.1° C. It dissolves readily in water, forming a solution having a specific gravity of 1.78 and containing 82 per cent. hydrobromic-acid gas.

60. Hydrogen Iodide.—Hydrogen iodide, HI, is prepared by methods similar to those according to which hydrogen bromide is prepared. Red phosphorus and iodine are mixed and placed in a dry flask, after which water is added to this mixture from a funnel, drop by drop, as was bromine in the preparation of hydrogen bromide. The equations expressing the reactions which take place may be written as follows:

$$P_4+10I_2+16H_2O=4H_3PO_4+20HI$$

Or, if a smaller proportion of iodine is used, the reaction will be:

$$P_4+6I_2+12H_2O=4H_3PO_3+12HI$$

61. Properties.—Hydrogen iodide, like hydrogen bromide, is a colorless gas with a specific gravity of 4.41; it has an acid reaction and fumes in the air. It easily condenses to a liquid by a pressure of 4 atmospheres at 0°; the liquid thus obtained boils at −35.6° C., and when cooled to −55° C. freezes to a clear, ice-like solid, which melts at −51.3° C. It is soluble in water, like hydrochloric-acid gas, yielding at 0° a solution of specific gravity 1.99. It is less stable than hydrogen bromide, as it gives up its hydrogen more readily; consequently, it cannot be prepared by the action of sulphuric acid on an iodide, for the hydrogen iodide set free is decomposed as fast as formed, depositing free iodine.

If allowed to stand, the solution of hydrogen iodide in water soon begins to decompose. The oxygen of the air combines with the hydrogen, forming water and setting free the iodine, which gives the solution a brown color:

$$4HI+O_2=2H_2O+2I_2$$

The easy oxidation of hydrogen iodide makes this compound a powerful reducing agent.

In organic chemistry, hydrogen iodide is very frequently employed for introducing hydrogen into a compound; for instance, by heating benzene with hydriodic acid, the benzene may be made to take up 6 atoms of hydrogen:

$$C_6H_6+6HI=C_6H_{12}+3I_2$$

Since the attraction of iodine for hydrogen is so feeble, a reaction does not occur between this halogen and hydrocarbons.

The fact that the organic compounds containing iodine are as a rule much less volatile and consequently more manageable than those of chlorine and bromine, leads to the extensive use of this element in researches on organic substances.

62. Hydrogen Fluoride.—Hydrogen fluoride, HF, is the most important compound of fluorine and is prepared either by the action of sulphuric acid on calcium fluoride, forming calcium sulphate and hydrogen fluoride, according to the equation:

$$\underset{\substack{\text{calcium}\\\text{fluoride}}}{CaF_2} + \underset{\substack{\text{sulphuric}\\\text{acid}}}{H_2SO_4} = \underset{\substack{\text{calcium}\\\text{sulphate}}}{CaSO_4} + \underset{\substack{\text{hydrogen}\\\text{fluoride}}}{2HF}$$

or by heating dry acid potassium fluoride, KHF_2, to redness in a platinum still.

63. Properties.—The hydrogen fluoride obtained as above is condensed to a colorless liquid that boils at 19.4° C., and has a specific gravity of .985 at 12°; it solidifies at −102° and melts at −92°. It has a most pungent, irritating odor which when inhaled in even small quantities causes serious irritation of the lungs. The acid corrodes the skin when brought in contact with it and creates painful ulcers.

Hydrofluoric acid, the aqueous solution of hydrogen fluoride, dissolves all metals except lead, gold, and platinum, and has only a slight action on magnesium. It decomposes the oxides of silicon and boron. When perfectly dry it has no action on glass, but the slightest trace of moisture causes it to decompose glass, the silica contained being dissolved according to the reaction:

$$SiO_2+4HF=SiF_4+2H_2O$$

Hydrofluoric acid decomposes metallic silicates, forming a metallic fluoride, which is in turn decomposed by either sulphuric or hydrochloric acid.

64. Etching Glass.—The etching action of hydrogen fluoride or its aqueous solution may easily be shown as follows: Coat thinly a small glass plate with wax or paraffin and after it has hardened, draw or write upon it with a sharp-pointed needle, taking care that the point of the needle has penetrated the wax or paraffin to the glass. Now place the glass plate wax side down over a small leaden dish containing hydrofluoric acid and allow it to remain for about 30 minutes. Then remove the plate, clean off the wax, and the writing or drawing will be etched into the glass.

Because of its action, it is, of course, impossible to ship hydrofluoric acid to the market in the ordinary glass carboy or container, but since the acid does not act on lead or wax, shipping containers are made from these materials. For laboratory use, the acid usually comes in 1-pound wax bottles.

OXYGEN ACIDS OF BROMINE AND IODINE

65. Those compounds of bromine and iodine with oxygen, which are well known, are very similar to the corresponding oxygen compounds of chlorine. The compounds formed by bromine are hypobromous acid, $HBrO$, and bromic acid, $HBrO_3$; there is also a possibility that the compound perbromic acid, $HBrO_4$, exists. It has never been isolated but its salts are known. Oxides of bromine do not exist.

The oxygen compounds of iodine which are well known are iodine pentoxide, I_2O_5; iodic acid, HIO_3, and periodic acid, H_5IO_6.

66. Hypobromous acid, $HBrO$, has not been prepared in a pure state because of its instability. A dilute solution of this acid may be made by agitating a cold aqueous solution of bromine with mercuric oxide:

$$HgO+2Br_2+H_2O=2HBrO+HgBr_2$$

Salts of hypobromous acid are prepared by a method similar to that used for the preparation of the hypochlorites. Bromine acting on a dilute solution of potassium hydroxide produces potassium hypobromite according to the equation:

$$2KOH+Br_2=KBr+KBrO+H_2O$$

Bromine vapor acting on calcium hydroxide (slaked lime) forms a compound similar to bleaching powder.

67. Bromic acid, $HBrO_3$, may be made in aqueous solution by means of the reaction between sulphuric acid and barium bromate:

$$Ba(BrO_3)_2+H_2SO_4=BaSO_4+2HBrO_3$$

The solution is removed from the barium sulphate by decantation and distilled under diminished pressure until its concentration reaches about 50 per cent. When this point is reached the acid decomposes, upon further heating, into water, bromine, and oxygen:

$$4HBrO_3=2Br_2+2H_2O+5O_2$$

Salts of bromic acid, such as potassium bromate and barium bromate, are made by treating aqueous solutions of the hydroxides of these metals with bromine:

$$6KOH+3Br_2=5KBr+KBrO_3+3H_2O$$

The chemical behavior of the bromates resembles to a certain extent that of the chlorates. Upon heating, however, bromates do not give rise to perbromates as do the chlorates, bromides being formed and oxygen evolved instead:

$$2KBrO_3=2KBr+3O_2$$

68. There is considerable doubt in regard to the existence of perbromic acid, $HBrO_4$. One investigator claims to have obtained it as an oily, colorless liquid by decomposing perchloric acid with bromine, but others have failed to get it by this or any other method.

69. Iodic acid, HIO_3, is similar to chloric and bromic acids, but is more stable. It may be prepared by methods similar to those used in the preparation of bromic acid, but is usually prepared by treating iodine with a strong oxidizing agent such as nitric acid:

$$I_2+10HNO_3=2HIO_3+10NO_2+4H_2O$$

It can also be obtained by passing chlorine through water in which iodine is suspended, when iodic and hydrochloric acids are formed according to the equation:

$$I_2+5Cl_2+6H_2O=2HIO_3+10HCl$$

Iodic acid is a white crystalline solid that decomposes into water and iodine pentoxide at 170° C., according to the equation:

$$2HIO_3=H_2O+I_2O_5$$

70. Iodine pentoxide, I_2O_5, is a white solid that is obtained by heating iodic acid to 170° C. It dissolves readily in water, forming iodic acid, and is therefore iodic anhydride, or the anhydride of iodic acid. It is the most stable of any of the compounds of the halogens with oxygen, but decomposes when heated to 300° C.

71. The normal periodic acid, HIO_4, is not known. The hydrate, $HIO_4{\cdot}2H_2O$, or H_5IO_6, is formed by the action of iodine on perchloric acid:

$$2HClO_4+I_2+4H_2O=2H_5IO_6+Cl_2$$

It is a solid crystalline body that fuses at 130° C., and decomposes at a higher temperature. Its salts are formed by oxidizing or heating iodates. The simplest way to prepare a periodate is to lead chlorine into a solution containing sodium hydroxide and sodium iodate, when the following reaction takes place:

$$3NaOH+NaIO_3+Cl_2=Na_2H_3IO_6+2NaCl$$

The salt $Na_2H_3IO_6$ is evidently derived from the acid H_5IO_6. From it the corresponding silver salt, $Ag_2H_3IO_6$, can be prepared; when this is treated with nitric acid it is converted into $AgIO_4$. The acid, HIO_4, is usually called periodic acid, and the compounds H_3IO_5 and H_5IO_6, which contain 1 and 2 molecules of water, respectively, are called hydrates. The fact that salts derived from these acids are known makes it appear probable that the oxygen and hydrogen are in the form of hydroxyl groups instead of in the form of water.

Periodic acid forms a remarkable series of salts which appear to be very complex, and correspond to the following formulas: HIO_4, $H_4I_2O_9$, H_3IO_5, H_5IO_6. These acids are known as meta-

periodic acid, diperiodic acid, mesoperiodic acid, and paraperiodic acid, respectively. Although salts having the formulas $M_8I_2O_{11}$ and $M_{12}I_2O_{13}$ have been described, they do not appear to be definite compounds. These are accounted for by the supposition of a hypothetical periodic anhydride, I_2O_7, from which the various acids are obtained by the addition of varying molecules of water, thus:

$$I_2O_7 + H_2O = 2HIO_4$$
$$I_2O_7 + 2H_2O = H_4I_2O_9$$
$$I_2O_7 + 3H_2O = 2H_3IO_5$$
$$I_2O_7 + 4H_2O = H_8I_2O_{11}$$
$$I_2O_7 + 5H_2O = 2H_5IO_6$$
$$I_2O_7 + 6H_2O = H_{12}I_2O_{13}$$

REVIEW OF THE HALOGENS

72. The elements fluorine, chlorine, bromine, and iodine form a closely allied group of non-metals, known as the halogens,

TABLE III
PHYSICAL PROPERTIES OF THE HALOGENS

Properties	Fluorine	Chlorine	Bromine	Iodine
Atomic weight.	19.00	35.46	79.92	126.92
Physical state.	Gas	Gas	Liquid	Solid
Melting point.	−233°	−102°	−7.3°	114.2°
Boiling point. .	−187°	−33.6°	58.7°	184.35°
Specific gravity	1.14*	1.55*	3.1883*	4.948†
Color of gas. . .	Pale-yellow	Greenish-yellow	Brownish-red	Violet

so called from the Greek words *hals*, meaning salt, and *gennao*, I produce.

A comparison of the physical and chemical properties and relations of the halogens and their compounds, brings out the

*Specific gravity of liquid.
†Specific gravity of solid.

following points, the physical properties being shown by Table III:

1. At ordinary temperatures, fluorine and chlorine are gases, bromine a liquid, and iodine a solid.

2. The specific gravity of the series increases regularly with fluorine as the lowest and iodine the highest, while the chemical activity diminishes with increase in specific gravity. Thus, the lightest element, fluorine, is the most active; iodine, the heaviest of the group, is the least active.

3. The ease with which the halogens combine with hydrogen decreases as the atomic weight increases. Thus, fluorine is again the most active and iodine the least active.

4. The ease with which the halogens combine with oxygen, on the other hand, increases as the atomic weight increases. Thus, fluorine does not combine at all while iodine forms the stable compound, iodine pentoxide.

5. The stability of the hydrogen compounds of the halogens decreases as the specific gravity increases, but with the oxygen compounds, it increases as the specific gravity increases. Hydrogen fluoride is more stable than hydrogen iodide. None of the oxides of chlorine are as stable as iodine pentoxide.

The relative affinities of the halogens may be illustrated by using one of them to set the other free from its compounds. Thus, fluorine will set chlorine, bromine, and iodine free from their compounds of sodium and other metals; chlorine will set bromine free and bromine will set iodine free:

$$2NaCl+F_2=2NaF+Cl_2$$
$$2NaBr+Cl_2=2NaCl+Br_2$$
$$2NaI+Br_2=2NaBr+I_2$$

If chlorine is introduced into a solution containing an iodide and a bromide, it first sets the iodine free and forms the corresponding chloride.

$$2KI+Cl_2+H_2O=2KCl+I_2+H_2O$$

When all the iodine is set free, the chlorine begins to oxidize it at the expense of the water and converts it all into iodic acid before any other reaction occurs.

$$I_2+6H_2O+5Cl_2=2HIO_3+10HCl$$

When all the iodine is converted into iodic acid, the chlorine sets the bromine free, and this colors the solution yellowish red.

$$2KBr + Cl_2 = 2KCl + Br_2$$

73. Preparation of Halogen Acids.—The usual method of preparing an acid is to treat a salt of that acid with a stronger acid, usually sulphuric acid. Hydrofluoric and hydrochloric acids are prepared in this way, but hydrobromic and hydriodic acids, on account of their instability, are more or less completely broken up by the sulphuric acid as fast as they are formed, and consequently cannot be obtained in this way. These two acids form the only notable exceptions to the general rule for preparing acids.

INORGANIC CHEMISTRY
(PART 7)

SULPHUR, SELENIUM, AND TELLURIUM

GENERAL REMARKS

1. The elements sulphur, selenium, and tellurium will be studied in this Section. Oxygen is really a member of this group (see Periodic Table), and as its atomic weight is the lowest, it would have been treated first in this Section had it not seemed advisable to consider it earlier in the Course. Sulphur, selenium, and tellurium, as well as oxygen, occur in allotropic modifications. The first three elements, however, are much more closely related to one another than to oxygen. In fact, the relation is somewhat like that which chlorine, bromine, and iodine bear to fluorine. For instance, they form compounds with oxygen, while oxygen forms no analogous compounds with them. Sulphur, selenium, and tellurium form with oxygen the compounds SO_3, SeO_3, and TeO_3, but oxygen does not form similar compounds with these elements. That is, the compounds OS_3, OSe_3, and OTe_3 do not exist. The valence of these elements toward hydrogen is 2, as shown by the compounds H_2O, H_2S, etc.

2. Oxygen and sulphur also form the compounds H_2O_2, hydrogen peroxide, and H_2S_2, hydrogen persulphide, respectively; little is known, however, of the constitution of the latter compound, and practically nothing of the valence of the sulphur in it. Toward the members of the halogen group the valence

of these elements ranges from 2 to 6. Toward oxygen, the other three members of this group are tetravalent and hexavalent.

Of the three elements, sulphur occurs in by far the largest quantity, selenium comes next, and tellurium occurs in relatively very small amounts. Selenium frequently accompanies sulphur in nature, and tellurium often occurs in combination with gold and silver. Selenium and tellurium also occur together combined with gold and silver.

SULPHUR

Symbol S. Atomic weight 32.06

3. **Occurrence.**—Sulphur, one of the earliest known elements, occurs free and in a combined state throughout nature in the neighborhood of active and extinct volcanoes. Its compounds occur in nature in much larger quantities and are more widely distributed than the free sulphur itself. Combined with the metals alone it forms sulphides or blendes, and with metals and oxygen it forms sulphates. Compounds of sulphur are also found in the vegetable and animal kingdoms.

Sulphur forms an essential part of the animal tissues as a constituent of albumin, fibrin, etc., and it exists also to a considerable extent in the tissues of vegetables and plants; its compounds cause the peculiar odor of garlic, mustard, etc. It is found mostly in volcanic regions, those bordering on the Mediterranean being particularly rich in it. Formerly the chief source of sulphur was Sicily, but the United States is now entirely supplied by the sulphur mines or wells of Louisiana and Texas, and a large quantity is also sold for export. The annual consumption of this material in this country was in 1919 about 673,000 tons. Sulphur is also found in commercial quantities in Iceland, New Zealand, Japan, and Mexico.

The most important naturally occurring compounds of sulphur are:

Sulphides: Iron pyrites, FeS_2; galena, PbS; blende, ZnS; cinnabar, HgS; stibnite, Sb_2S_3; realgar, As_2S_2; orpiment, As_2S_3; copper pyrites, $CuFeS_2$.

Sulphates: Gypsum, $CaSO_4 \cdot 2H_2O$; celestite, $SrSO_4$; heavy spar, $BaSO_4$; green vitriol, $FeSO_4 \cdot 7H_2O$; Glauber's salt, $Na_2SO_4 \cdot 10H_2O$; Epsom salts, $MgSO_4 \cdot 7H_2O$.

4. Preparation.—Commercial sulphur is the native material in a purified state; the native sulphur is commonly distributed in veins through masses of gypsum and celestite which must be separated from the sulphur by heat. This is accomplished by placing the native material in a row of earthen jars A, Fig. 1, heated by a long furnace, and provided with narrow tubes that convey the sulphur vapor into a second row of jars B that, standing outside of the furnace, act as receivers

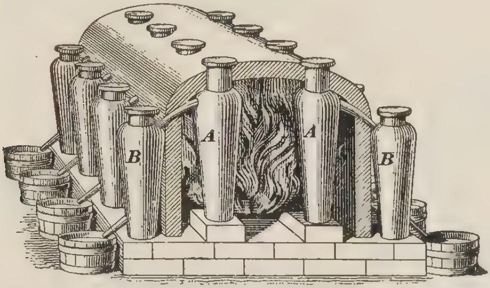


FIG. 1

and condense the sulphur vapor into the liquid state and from which it flows into vessels of water.

5. The sulphur thus obtained is exported as rough sulphur, and contains between 3 and 4 per cent. of earthy impurities which must be removed by distillation. This redistilling, or refining process, is done in the apparatus shown in Fig. 2. A cast-iron cylinder A receives the melted sulphur from a tank C which is heated by the waste gases of the furnace. The sulphur vapor enters a large brick chamber B the floor of which is slightly inclined, so that the condensed liquid sulphur may flow toward a tap H which can be opened when necessary. A damper R which is regulated by a chain, permits the closing or opening of the cylinder A. The brick chamber B is provided with a safety valve K, which permits the escape of the expanded air.

At first when the walls of the brick chamber are cold, the sulphur vapors condense in the form of a fine powder known as flowers of sulphur; but when the walls of the chamber become thoroughly heated the sulphur vapors condense to a liquid which when the tap *H* is opened, is drawn into a vessel *E* and ladled into cylindrical molds where it soon solidifies and forms the commercial product known as brimstone.

6. Frasch Process for Mining Sulphur.—In Louisiana sulphur is mined by the Frasch process, which consists essen-

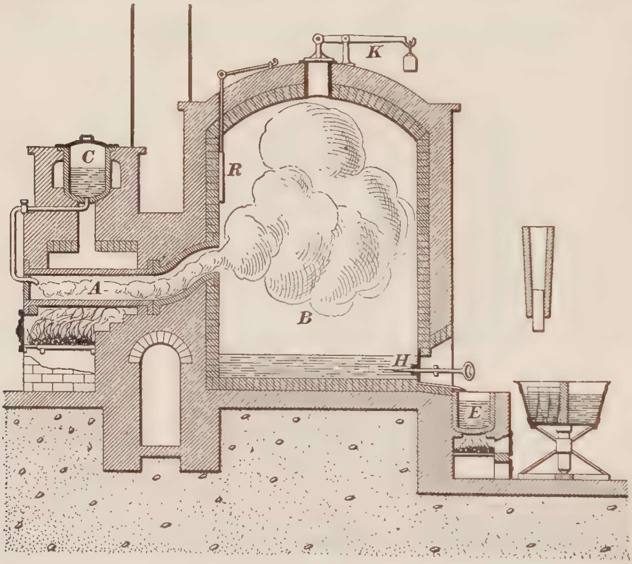


FIG. 2

tially of melting the sulphur below the surface by means of superheated water and then raising the molten sulphur to the surface by means of compressed air. The process may be described as follows:

A well 17 inches in diameter is bored to a depth of about 50 feet. Through this well a wrought-iron pipe 13 inches in diameter is sunk to a variable depth, sometimes as much as 250 feet. This pipe acts as a casing. Inside of the 13-inch pipe an 8-inch pipe is sunk to the bottom of the sulphur bed and in order to prevent plugging of the pipe at the bottom that

portion of it which is immersed in the sulphur is perforated, the holes being arranged in spiral form and about 6 inches apart. By means of this arrangement the hot water led to the sulphur bed through this pipe has access to the sulphur throughout the entire thickness of the deposit, and if the bottom of the pipe should become stopped no trouble would be caused by reason of the perforations at the bottom of the pipe. Inside the 8-inch pipe a 6-inch pipe is sunk to the bottom of the sulphur bed, hot water being also pumped down this pipe. Inside the 6-inch pipe a 3-inch pipe is driven down to the sulphur bed and it is through this pipe that the molten sulphur reaches the surface. Finally inside this 3-inch pipe a 1-inch pipe is driven down to the sulphur and it is through this pipe that the compressed air is forced.

7. Superheated water is pumped down the 8-inch and 6-inch pipes, the water from the 8-inch pipe melting the sulphur, which sinks down to the bottom of the sulphur bed. The hot water in the 6-inch pipe serves to keep the sulphur in the 3-inch pipe in a molten condition on its way to the surface. When sufficient sulphur has been melted, and this is determined by practice, compressed air at a pressure of 250 pounds per square inch is forced down the 1-inch pipe and the liquid sulphur is pushed to the surface through the 3-inch pipe. Upon reaching the surface the sulphur is conducted to roughly constructed bins, where it soon solidifies.

The sulphur produced by this method of mining has a purity ranging from 99.93 to 99.98 per cent. and contains very little water, if any. The Frasch process, however, can only be applied where the deposit is very rich in sulphur, and for this reason, it has only been used with success in Louisiana and Texas and not in other parts of the world.

8. In Sweden, Germany, and France sulphur is obtained by distilling iron pyrites. This method depends on the following decomposition of iron pyrites:

$$3FeS_2 = Fe_3S_4 + 2S$$

This decomposition is usually effected in a kiln similar to a lime kiln having an opening in the side into which a wooden

trough is fastened. A small quantity of fuel is lighted on the bars of the furnace and the kiln is filled with the pyrites. The burned pyrites is removed from time to time from the bottom and fresh material is added on top. About half of the sulphur burns away and the rest is volatilized.

Another source of sulphur is the residue or waste in the manufacture of soda. This waste material consists of calcium sulphide mixed with lime, chalk, and some alkali sulphides. The waste is treated with carbonic-acid gas in the presence of water when hydrogen sulphide and calcium carbonate are formed:

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S$$

The gas thus obtained is brought into contact with heated ferric oxide when the following reaction takes place:

$$2H_2S + 2Fe_2O_3 = 4FeO + 2S + 2H_2O$$

The sulphur formed is condensed in cooling chambers and recovered in a pure state.

9. **Physical Properties.**—Sulphur exists in two distinct solid and liquid forms. In its ordinary form, it has a characteristic lemon-yellow color; it is insoluble in water; it may be called tasteless, but possesses a faint odor. Its rolls are extremely brittle. As it is at the same time a very bad conductor of heat, the warmth of the hand is frequently sufficient to cause the roll to fall in pieces. This phenomenon may be explained by the fact that freshly made roll sulphur consists of a mass of oblique prismatic crystals but, after being kept for some time it consists of octahedra. This change in the structure of the mass taking place when its solid condition prevents the free movement of the particles, gives rise to a state of internal tension, and causes this extreme brittleness. The warmth of the hand causes an unequal expansion of the roll of sulphur; or, in other words, it causes an increased movement of its particles in that part of the roll that is directly exposed to the human heat, which results in a breaking up of the mass.

Crystals of native sulphur, as well as those obtained by the evaporation of a solution, belong to the rhombic system

of crystallization, illustrated in Fig. 3. Rhombic sulphur includes both roll sulphur and flowers of sulphur and this variety is stable at temperatures below 96° C.; above this temperature it changes slowly to monoclinic sulphur. Rhombic sulphur melts at 114.5° C.

10. When melted sulphur is allowed to cool slowly, long, prismatic, needle-like crystals are deposited, of the form shown in Fig. 4, which melt at 119.25° C. These crystals, which are known as monoclinic sulphur, are at first perfectly transparent, but after a short time become entirely opaque by each breaking up into a number of minute rhombic crystals. Monoclinic sulphur may be prepared in the laboratory by heating a small iron or clay crucible half-filled with sulphur over a small flame. Care should be taken that the sulphur does not take fire. When all of the sulphur has been melted, the flame is removed, and as the sulphur cools a crust forms on its surface. If this crust is pierced at two opposite points near the edge, the melted sulphur remaining in the crucible may be poured out. On removing the crust, it will be noticed that the crucible contains a mass of long, transparent needles, or prisms. Monoclinic sulphur can only be kept as such at a temperature above 96° C., and below its melting point, 119.25° C.

FIG. 3

FIG. 4

11. If sulphur is dissolved in carbon disulphide and the liquid allowed to evaporate, the sulphur is obtained in crystals of the rhombic system. These are permanent in air and the form is that in which the native sulphur crystals occur. If sulphur is heated above its melting point and the application of heat is continued, a remarkable series of changes ensue. The color gradually darkens as the temperature rises; at the same time the liquid becomes thicker until at a temperature near 160° C. the mass is almost black and so viscous that the vessel may be inverted without causing the sulphur to run out. With a further increase in temperature beyond 260° C., the sulphur again becomes liquid but remains much thicker than when first melted. If in this state it is poured into cold water, a soft,

rubber-like sulphur of an allotropic variety, known as plastic sulphur, is obtained. The difference between this variety and the common brittle form of sulphur is very striking. In about an hour, however, at 100° C., it loses its tenacity and again becomes opaque and brittle. All varieties of sulphur boil at 444.6° C.

12. Chemical Properties.—Chemically sulphur is an active element. When metals with the exception of gold and platinum in a very finely divided state are intimately mixed and rubbed together with powdered sulphur, at ordinary temperatures a reaction takes place and the sulphides of the metals are produced. Thus:

$$2Ag+S=Ag_2S$$

Most metals when heated with sulphur combine energetically, the sulphides of the metals again being formed. Sulphur also unites with non-metals such as chlorine and oxygen, to form chlorides and oxides, respectively. Sulphur is slowly oxidized to sulphuric acid by the oxygen of the air in conjunction with atmospheric moisture:

$$2S+2H_2O+3O_2=2H_2SO_4$$

13. Tests.—In the free state sulphur may be easily recognized by its color, its volatility when heated, and its characteristic odor when burned. When sulphur is combined as a soluble sulphide of sodium or potassium by fusion of elemental sulphur, metallic sulphides or sulphates, with sodium or potassium carbonate and carbon, in an iron crucible, the soluble sulphide which is formed blackens paper moistened with a solution of lead acetate. This color is due to the formation of lead sulphide, PbS:

$$\underset{\text{lead acetate}}{Pb(C_2H_3O_2)_2}+Na_2S=PbS+\underset{\text{sodium acetate}}{2NaC_2H_3O_2}$$

14. Uses.—Sulphur finds extensive employment in the arts and in various manufacturing and industrial processes such as the manufacture of sulphuric acid, carbon bisulphide, gunpowder, and sulphur dioxide, in which form it serves as a bleaching agent. Sulphur and sulphur compounds are also used to a great extent in paper and rubber industries.

15. Sulphur Molecule.—As the result of experimental work undertaken to determine the atomicity of the sulphur molecule, it is now concluded that the atomicity and likewise the molecular weight of sulphur varies at different temperatures. Thus, at about 500° C., the molecule contains 6 atoms of sulphur; it is therefore hexatomic at this temperature and the molecular formula may be written S_6. On increasing the temperature to 1,000° C., the molecule becomes diatomic and is written S_2; at 2,000° C., there is evidence to show that the molecule, partially at least, dissociates into atoms of S. It is also possible that at temperatures between 500° C. and 1,000° C., some or all of the molecules S_2, S_4, S_6, and S_8 are present. Because of the variation of the atomicity of the sulphur molecule with the temperature, only the symbol for sulphur, S, will be employed in writing chemical equations.

HYDROGEN SULPHIDE

Formula H_2S. Molecular weight 34.076

16. History and Occurrence.—Hydrogen sulphide, also known as sulphureted hydrogen, was discovered by Scheele in the year 1777. It occurs in certain volcanic gases and is the essential constituent of the water of the so-called sulphur springs among the best known of which are Sharon and Avon in the United States; Harrowgate in England; Aix-la-Chapelle in Germany; and Bagnères in France. It is found in the gas of eggs and sewers, and is produced by the putrefaction of animal and vegetable matter.

17. Preparation.—In the laboratory the gas is generated by the action of either dilute hydrochloric acid or dilute sulphuric acid on ferrous sulphide. The latter, although it is usually purchased for use, may be prepared by strongly heating a mixture of iron and sulphur.

$$Fe+S=FeS$$

The generation of hydrogen-sulphide gas is a very simple matter, but difficulty is sometimes encountered by overlooking

certain precautions which should be taken and which are included in the following directions:

A small quantity (a half-dozen lumps, or pieces, approximately the size of a pea) of ferrous sulphide is placed in the bottle *a*, Fig. 5, and the apparatus is then connected as shown. At *e e*, the connections are made by means of rubber tubing and at *f f* by means of rubber stoppers. All connections must be gas-tight. Dilute hydrochloric acid (about 1 part acid to 3 parts water) or dilute sulphuric acid (1 part acid to 6 parts water) is now poured down the funnel or thistle tube *d*, which enters the bottle *a*. It should be noted

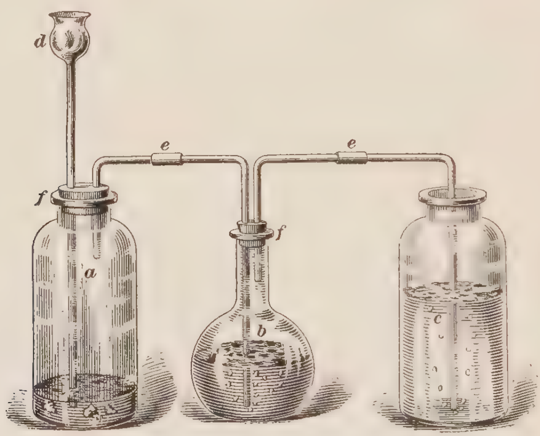


Fig. 5

that the thistle tube reaches very close to the bottom of the bottle (about $\frac{1}{8}$ inch above the bottom) and just enough acid is added to cover the ferrous sulphide and to reach above the bottom of the thistle-tube stem in order to prevent the escape of the gas through the tube. Thus, the acid acts as a liquid seal. When the dilute acid comes in contact with the ferrous sulphide, hydrogen-sulphide gas is immediately generated. The gas is then led through the flask *b*, which contains water through which the gas bubbles and is washed. From the wash bottle the gas is then passed into the bottle *c*, which contains water or ammonium hydroxide, depending upon whether ammonium sulphide or a solution of the gas in water is desired.

If a solution is to be tested, a few cubic centimeters are placed in a test tube and the gas passed through it.

18. As hydrogen-sulphide gas is very poisonous, it should be generated only as just described, under a hood or in a well-ventilated room. By using a very little acid at one time, excessive generation of the gas can be avoided. If it is desired to stop the evolution of the gas, the acid may be poured off into a drain and the unused ferrous sulphide allowed to remain in the flask.

The following reactions take place in the preparation of hydrogen-sulphide gas:

$$FeS + 2HCl = H_2S + FeCl_2$$
$$FeS + H_2SO_4 = H_2S + FeSO_4$$

19. For the continuous preparation of hydrogen sulphide from ferrous sulphide and dilute sulphuric or hydrochloric acid, in the larger laboratories, Kipp's apparatus, shown in Fig. 6, is very convenient. It consists of three glass bulbs, the two lower ones A and B being in a single piece, and the upper one C prolonged by a tube D reaching to the bottom of the lowest one, being ground air-tight into the neck of the second. Through the tubulure E, the ferrous sulphide is introduced in fragments about the size of a chestnut, the space between the tube and the side of the constriction being too narrow to let them drop into the bulb A. This tubulure E is

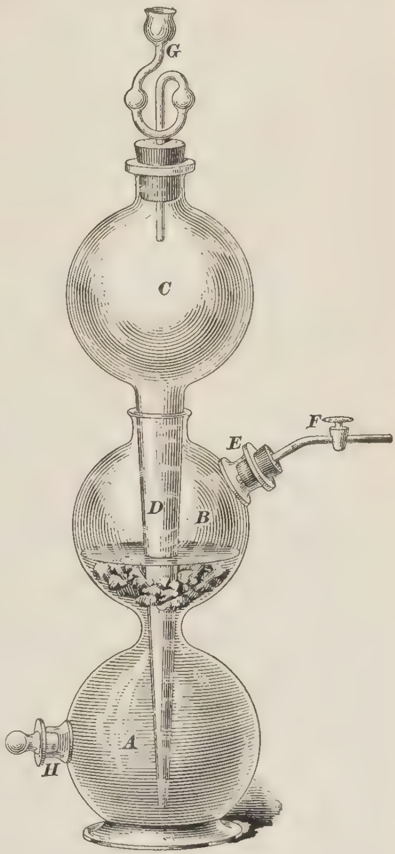


FIG. 6

then closed by a stopper through which a glass tube with a stop-cock F passes. The diluted acid (in the proportion of 1 part of acid to 9 parts of water) is poured through the opening G in the bulb C and runs into the bulb A and rises to overflow the iron sulphide in bulb B. If the stop-cock F is open, the evolved gas escapes; but when it is shut the pressure of the accumulating gas forces the liquid away from the sulphide down into the bulb A and thence back into bulb C, thus stopping the action of further generating and at the same time preserving a certain volume of hydrogen sulphide always ready when required. The acid when saturated is removed through the tubulure H.

20. Physical Properties.—Hydrogen sulphide is a colorless gas having the characteristic odor of rotten eggs. It is heavier than air, having a specific gravity of 1.18 at 15° C. Cooled to −74° C., or submitted to a pressure of 17 atmospheres at 10° C., it condenses to a colorless liquid having a specific gravity of .90. This liquid freezes to a solid at −83.8° C., and boils at −60.2° C. It is soluble in water, 1 part dissolving 4.37 parts of the gas at 0° C.; at 40° C., the solubility of the gas is much less, 1 part of water dissolving only 1.86 parts of the gas, which may be completely expelled from a solution by boiling. The gas is very poisonous and when being used or generated in the laboratory the work should be carried out under a hood in order that any gas which escapes may pass out of the room. If a hood is not available the room should be well ventilated, but under no circumstances should a person breathe air contaminated by this gas for any length of time.

21. Chemical Properties.—In water solution, the gas shows the properties of a weak acid, turning blue litmus paper red, and for this reason it is also called hydrosulphuric acid. It is easily decomposed into hydrogen and sulphur at 400° C.

$$2H_2S = 2H_2 + 2S$$

Hydrogen sulphide is not a supporter of combustion but it will burn in an adequate supply of air with a blue-colored flame, sulphur dioxide and water being formed.

$$2H_2S+3O_2=2SO_2+2H_2O$$

The gas reacts with metals and their oxides to produce sulphides, setting hydrogen free in the first case and water in the second. In the form of a gas or in solution it is converted into water and sulphur by oxidizing agents.

$$2H_2S+O_2=2H_2O+2S$$

It is also attacked by the halogens, sulphur being set free and the corresponding halogen acid being formed:

$$H_2S+Cl_2=2HCl+S$$

The affinity possessed by hydrogen sulphide for oxygen enables it to remove the latter from its compounds, thus acting as a reducing agent.

Common examples of the action of hydrogen sulphide are seen in the tarnishing of silver ornaments and utensils due to the presence of the gas in the air. The blackening of lead is also due to this cause.

22. The Acidity of Hydrogen Sulphide.—The acid properties of an aqueous solution of hydrogen sulphide have already been mentioned. These are however so feeble that in the case of soluble sulphides carbon dioxide is able to displace the hydrogen sulphide. The sulphides of all the metals are insoluble in water with the exception of those of calcium, barium, strontium, magnesium, sodium, and potassium, and a few of the very rare metals. The insolubility of the other metallic sulphides affords the analyst a very valuable means of separating those metals from the above-mentioned group. Whenever the compounds are brought together which contain elements that, by their union, are capable of forming an insoluble compound, that compound as a rule will be formed; so that, although hydrogen sulphide is rather a weak acid, it is able to displace stronger ones from many metals. A current of hydrogen sulphide passed through a solution of copper chloride precipitates copper sulphide according to the equation:

$$\underset{\text{copper chloride}}{CuCl_2} + \underset{\text{hydrogen sulphide}}{H_2S} = \underset{\text{copper sulphide}}{CuS} + \underset{\text{hydrochloric acid}}{2HCl}$$

although hydrochloric acid is a much stronger acid than is H_2S.

These sulphides have in many cases very characteristic colors by which they may be readily recognized. They possess further the advantage of being divided into two distinct groups, namely into one group that is soluble in dilute hydrochloric acid, and into one that is insoluble in this agent.

Typical reactions of hydrogen sulphide with acid and alkaline solutions of different salts are represented by the following equations.

In acid solution:

$$\underset{\text{copper sulphate}}{CuSO_4} + \underset{\text{hydrogen sulphide}}{H_2S} = \underset{\text{sulphuric acid}}{H_2SO_4} + \underset{\text{copper sulphide}}{CuS} \quad \text{(black)}$$

$$\underset{\text{antimony chloride}}{2SbCl_3} + \underset{\text{hydrogen sulphide}}{3H_2S} = \underset{\text{hydrochloric acid}}{6HCl} + \underset{\text{antimony sulphide}}{Sb_2S_3} \quad \text{(orange)}$$

In alkaline solution:

$$\underset{\text{zinc sulphate}}{ZnSO_4} + \underset{\text{hydrogen sulphide}}{H_2S} = \underset{\text{sulphuric acid}}{H_2SO_4} + \underset{\text{zinc sulphide}}{ZnS} \quad \text{(white)}$$

Compounds are also formed in which only 1 hydrogen atom of the H_2S is replaced by a metal. These are known as hydrosulphides. Common examples are sodium hydrosulphide, $NaHS$, and potassium hydrosulphide, KHS.

23. Decomposition of Hydrogen Sulphide.—The existing great affinity between hydrogen and chlorine leads to the decomposition of hydrogen sulphide, as has been previously shown.

Free oxygen has no action on the dry gas but in the presence of water a slow oxidation takes place. Hence, an aqueous solution of hydrogen sulphide becomes turbid on exposure to the atmosphere through the separation of sulphur and the formation of water, thus:

$$2H_2S + O_2 = 2S + 2H_2O$$

24. Tests.—Hydrogen sulphide is easily detected by placing in it a piece of paper moistened with a solution of lead acetate; in this way it may be shown to exist in most specimens of coal gas and in the gaseous exhalations from drains, cesspools, etc. With sodium nitroferricyanide, $Na_2Fe(CN)_5NO$

$\cdot 2H_2O$, in alkaline solution, it gives a deep-purple color due to the formation of sodium nitroferrocyanide, $Na_3Fe(CN)_5NO \cdot 2H_2O$:

$$2Na_2Fe(CN)_5NO \cdot 2H_2O + Na_2S = 2Na_3Fe(CN)_5NO \cdot 2H_2O + S$$

25. Hydrogen Persulphide.—Hydrogen persulphide, H_2S_2, was first prepared by Scheele and completely investigated by Berthollet. It is prepared by adding a clear, well-cooled solution of calcium pentasulphide, CaS_5, to dilute hydrochloric acid:

$$2CaS_5 + 4HCl = 2H_2S_2 + 2CaCl_2 + 6S$$

It separates as a heavy, yellowish oil possessing a characteristic pungent smell and a specific gravity of 1.734. It is practically insoluble in alcohol but dissolves readily in carbon bisulphide and benzene. It decomposes slowly when dry and away from the air, into hydrogen sulphide and free sulphur. Water and heat hasten the decomposition.

OXIDES AND ACIDS OF SULPHUR

26. Sulphur forms the following series of oxides and acids:

Sulphur dioxide, SO_2	Hyposulphurous acid, $H_2S_2O_4$
Sulphur trioxide, SO_3	Sulphurous acid, H_2SO_3
	Sulphuric acid, H_2SO_4

SULPHUR DIOXIDE

Formula SO_2. Molecular weight 64.06

27. History and Occurrence.—Attention was first called to sulphur dioxide by the alchemist Stahl, but not until 1774 did Priestley carefully investigate this compound and its properties. Sulphur dioxide is rarely found in nature. It exists, however, in gases issuing from volcanoes. Although constantly discharged into the air of towns by the combustion of coal (which always contains more or less sulphur), it is so easily oxidized and converted into sulphuric acid that no considerable quantity is ever found in the atmosphere.

28. Preparation.—When sulphur is burned in air or pure oxygen, sulphur dioxide and sulphur trioxide are formed. In air the latter is formed to the extent of 6 per cent. to 8 per cent. However, if the sulphur is burned in pure oxygen, only from 2 per cent. to 3 per cent. of sulphur trioxide is formed, indicating that some element which is present, probably nitrogen, acts as a catalytic agent in the formation of sulphur trioxide. The equations representing the formation of these oxides of sulphur may be written thus:

$$(1)\quad S+O_2=SO_2$$
$$(2)\quad 2SO_2+O_2=2SO_3$$

When needed for laboratory use it is generally prepared in small quantities by heating sulphuric acid with metallic copper, according to the following directions:

Twenty grams of copper clippings is heated in a flask with 110 cubic centimeters of strong sulphuric acid, the gas being conducted by a bent tube down to the bottom of a dry bottle closed with a perforated card. Some time will elapse before the gas is evolved, for sulphuric acid acts upon the copper only at a high temperature; but when the evolution of the gas fairly commences it will proceed very rapidly, so it is necessary to remove the flame from under the flask. The gas will contain a little suspended vapor of sulphuric acid which makes it turbid.

The reaction which takes place is rather complicated but is usually represented thus:

$$\underset{\text{sulphuric acid}}{2H_2SO_4} + \underset{\text{copper}}{Cu} = \underset{\text{copper sulphate}}{CuSO_4} + \underset{\text{water}}{2H_2O} + \underset{\text{sulphur dioxide}}{SO_2}$$

Pure sulphur dioxide is also prepared by treating a sulphite with dilute sulphuric acid, thus:

$$Na_2SO_3+H_2SO_4=Na_2SO_4+H_2O+SO_2$$

and also by heating together sulphuric acid and sulphur:

$$2H_2SO_4+S=3SO_2+2H_2O$$

On a large scale it is prepared by heating carbon and sulphuric acid together. Carbon dioxide is also evolved, but this is not detrimental when the sulphur dioxide is used for the

manufacture of sulphites. The equation representing this reaction is:

$$C+2H_2SO_4=2SO_2+CO_2+2H_2O$$

29. Physical Properties.—Sulphur dioxide is a heavy, colorless gas with a pungent suffocating odor resembling that of a burning sulphur match. It is more than twice as heavy as air, its specific gravity being 2.23. Cooled to $-10°$ C., it condenses to a thin, colorless liquid with a specific gravity of 1.49; this liquid freezes at $-76.1°$ C.

The gas is very soluble in water, one part of which dissolves 797.9 volumes at 0° C. and 156 volumes at 50° C. The solution may be completely freed from the gas by boiling.

30. Chemical Properties.—Sulphur dioxide is a stable gas, being decomposed only at high temperatures. The dry gas itself does not show an acid reaction with litmus, but its solution in water is decidedly acid.

$$SO_2+H_2O=H_2SO_3 \text{ (sulphurous acid)}$$

The equation shows that it is the anhydride of sulphurous acid. The gas is poisonous when inhaled, due to the absorption of sulphur dioxide by the blood, with subsequent oxidation to sulphuric acid. The moist gas is a strong bleaching agent. It is quite soluble in water and its solution dissolves phosphorus, sulphur, iodine, bromine, and many gases. Sulphur dioxide has a great affinity for oxygen and is slowly oxidized to sulphur trioxide.

Sulphur dioxide is used as a disinfecting, bleaching, and refrigerating agent. For convenient use it may be purchased under pressure in steel cylinders.

31. Sulphurous Acid.—When sulphur dioxide is passed into water, it goes into solution and forms sulphurous acid, H_2SO_3. This acid is very unstable and has never been isolated, its solution in water only being known. The acid being dibasic, forms normal and acid salts, like Na_2SO_3, normal sodium sulphite, and $NaHSO_3$, acid sodium sulphite.

Sulphurous acid is a good bleaching agent, being extensively used for this purpose where delicate fabrics would be destroyed by the stronger action of bleaching powder.

32. Hyposulphurous Acid. — Hyposulphurous acid, $H_2S_2O_4$, was first obtained by a German chemist named Schutzenberger by reducing sulphurous acid by means of zinc, thus:

$$3H_2SO_3+Zn=ZnSO_3+H_2S_2O_4+2H_2O$$

As a result of the above reaction, a yellow solution results which possesses a strong bleaching power. The acid combines readily with oxygen and is a more active reducing agent than is sulphurous acid.

A salt of hyposulphurous acid may be prepared by the action of zinc on a solution of sodium acid sulphite which contains an excess of sulphur dioxide,

$$2NaHSO_3+Zn+SO_2=Na_2S_2O_4+ZnSO_3+H_2O$$

SULPHUR TRIOXIDE

Formula SO_3. Molecular weight 80.06

33. Preparation.—Sulphur trioxide, or sulphuric anhydride, is prepared by passing a mixture of sulphur dioxide and oxygen over heated platinum sponge. Platinized asbestos may be used in place of the pure platinum sponge. The apparatus

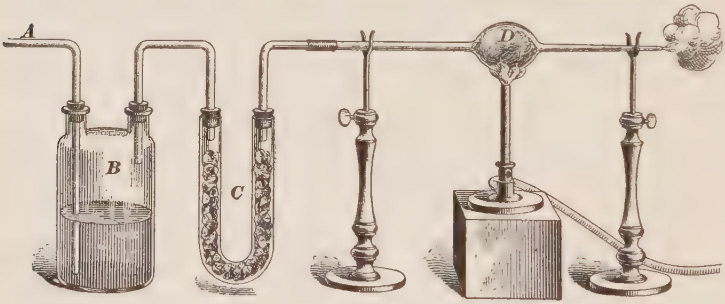


FIG. 7

shown in Fig. 7 may be used to show the preparation of sulphur trioxide from sulphur dioxide. Oxygen is led through the tube A through a strong solution of sulphurous acid contained in B. Here the oxygen takes up sulphur dioxide and the mixture is passed through pumice stone in C soaked with sulphuric

acid to remove all traces of moisture from the mixture, and then passed over the heated platinized asbestos in *D*.

Platinized asbestos may be obtained by wetting some asbestos with a solution of platinic chloride and heating this to redness, whereby the platinum is reduced to the metallic state, thus covering the asbestos with a thin film of platinum.

34. Physical Properties.—Sulphur trioxide exists in two distinct varieties or forms distinguished by the Greek names of the letters *a* and *b*, or sometimes by the corresponding Greek letters, α and β, *alpha* and *beta*. The alpha variety is a colorless liquid with a specific gravity of 1.9229. It solidifies at 16.8° and boils at 44.88°. In contact with air it fumes strongly and minute drops of sulphuric acid are formed.

$$SO_3 + H_2O = H_2SO_4$$

The beta variety probably has the formula $(SO_3)_2$; it exists in the form of silky needles resembling asbestos. It has a specific gravity of 1.04 and melts at 50° C.

35. Chemical Properties.—On passing sulphur trioxide through a red-hot tube, it decomposes into oxygen and sulphur dioxide.

$$\underset{\text{sulphur trioxide}}{2SO_3} = \underset{\text{sulphur dioxide}}{2SO_2} + \underset{\text{oxygen}}{O_2}$$

Sulphur trioxide unites readily with water with the evolution of great heat, producing sulphuric acid.

$$\underset{\text{sulphur trioxide}}{SO_3} + \underset{\text{water}}{H_2O} = \underset{\text{sulphuric acid}}{H_2SO_4}$$

SULPHURIC ACID

Formula H_2SO_4. Molecular weight 98.076

36. History and Occurrence.—The discovery of sulphuric acid or oil of vitriol as it is sometimes called, dates back more than four centuries; it was first prepared by an alchemistically inclined monk, Basil Valentine, in the 15th century, who called it *oleum sulphuris per campanum*. Dr. Roebuck, an

Englishman, proposed the present method of manufacture in 1770. The acid thus prepared is therefore often called English sulphuric acid.

Sulphuric acid occurs free to a remarkable extent in river and spring waters. Boussingault, a French chemist, estimates that the Rio Vinagre in South America carries daily to the sea more than 38,000 kilograms of the acid; and that the water of the Oak Orchard mineral spring, New York, contains in each liter about 2.5 grams.

Not only is it found in water but also in the animal and mineral kingdoms. It has been observed as a secretion of certain mollusks and is found in the sulphates of iron, calcium, barium, and strontium, forming the minerals melanterite, gypsum, barite, and celestite.

37. Importance of Sulphuric Acid.—There is no substance, with the single exception of water, that is so important to the manufacturing or analyzing chemist as sulphuric acid. The frequency of its application to various purposes in the preceding experiments will give some idea of its usefulness and a familiarity with its properties, etc.

38. Preparation.—Sulphuric acid is manufactured on an immense scale in this country and is never prepared in the laboratory for actual use, but is always purchased. A detailed description of the present process of manufacture will be very easily understood after a consideration of the chemical changes on which it depends.

Sulphur dioxide is produced by burning sulphur in the air, thus:

$$\underset{\text{sulphur}}{S} + \underset{\text{oxygen}}{O_2} = \underset{\text{sulphur dioxide}}{SO_2}$$

When sulphur dioxide is treated with an oxidizing agent in the presence of water it is converted into sulphuric acid, thus:

$$SO_2 + H_2O + O = H_2SO_4$$

In practice the oxidation is principally accomplished by a mixture of nitric oxide and nitrogen peroxide, NO and NO_2, which acts like nitrogen trioxide, N_2O_3, and is so written in the

following equations. In starting the process nitric acid is used as the oxidizing agent instead of nitrogen trioxide. The reaction is as follows:

$$2HNO_3+2SO_2+H_2O=2H_2SO_4+N_2O_3$$

After this the oxidation is accomplished principally by N_2O_3, and the principal reactions are the formation of nitrosyl sulphuric acid, NO_2OHSO_2, and the decomposition of this compound by water with the formation of sulphuric acid. These reactions are usually represented by the equations:

$$2SO_2+N_2O_3+O_2+H_2O=2NO_2OHSO_2$$
$$2NO_2OHSO_2+H_2O=2H_2SO_4+N_2O_3$$

Chamber Proces

39. The nitrogen trioxide formed in the second reaction serves to oxidize a second portion of sulphur dioxide, so that

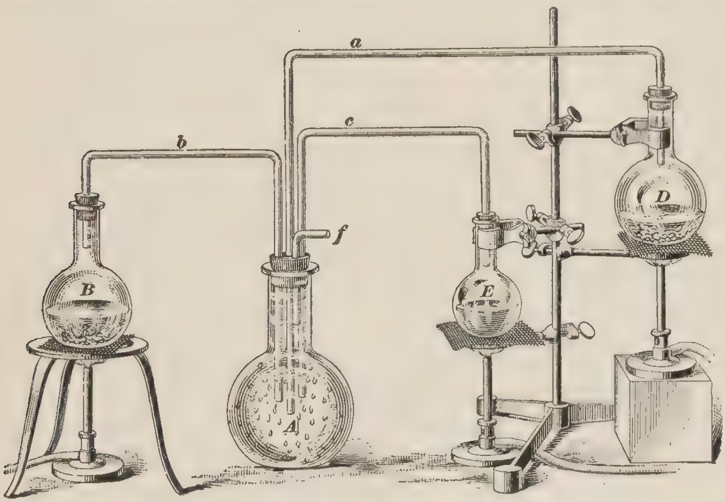


FIG. 8

theoretically a small quantity of this gas should be capable of oxidizing an indefinite quantity of sulphur dioxide, and in modern plants the waste of nitrogen trioxide is but slight.

The chemical principles illustrating the manufacture of sulphuric acid are shown in Fig. 8 and will aid in giving a clear understanding of the process employed in manufacturing sulphuric acid on a large scale.

40. A large Florence flask A, Fig. 8, is fitted with a stopper through which several tubes pass: a tube a connected with a flask D containing copper and strong sulphuric acid for evolving SO_2; a tube b connected with the flask B containing copper and dilute nitric acid for supplying nitrogen dioxide; a tube c connected with a small flask E containing water; a tube f for supplying air and preventing the pressure in A rising above that of the atmosphere. On heating the flask B, nitric oxide passes over into flask A, the greater part combining with the oxygen of the air and being converted to nitrogen peroxide. Flask A then contains a mixture of NO and NO_2. Flask D is then heated, when sulphur dioxide is evolved. This passes over into the flask A and decolorizes the red gas, nitrosyl sulphuric acid being formed. The heat is then removed from the flask D, and steam is generated in flask E and sent into flask A, the nitrosyl sulphuric acid being decomposed and sulphuric acid formed.

COMMERCIAL MANUFACTURE OF SULPHURIC ACID

41. Lead-Chamber Process.—The lead-chamber process consists essentially in bringing together under suitable conditions sulphur dioxide, oxygen, and water, in the presence of the oxides of nitrogen, with the resultant formation of sulphuric acid. The reactions that actually take place between these substances in the chamber are rather obscure, although the final result is as though the reaction was $SO_2+O+H_2O=H_2SO_4$; that is, as though the oxides of nitrogen did not react. However, it is known that this reaction will not take place in the chamber without the presence of the nitrogen oxides. In practice much more water is needed to bring about the reaction than is theoretically required for the production of H_2SO_4. The sulphuric acid formed in chambers is therefore always dilute. The theory as to the chemistry of the reactions is given briefly below.

For the manufacture of sulphuric acid by the chamber process besides the burners, flues, dust chambers, etc., there are three principal elements—(1) the Glover towers, (2) the acid

chambers, and (3) the Gay-Lussac towers. In most plants the niter pots, or retorts, may also be considered one of the principal elements.

42. Sulphur dioxide is produced by burning sulphur or more cheaply by roasting sulphur ores, such as iron pyrites, FeS_2, in a suitable furnace called a burner, a mixture of air and sulphur dioxide being obtained.

The gases coming from the pyrite or sulphur burners usually contain 5 to 8 per cent. sulphur dioxide; a small proportion, usually less than 0.5 per cent., of sulphur trioxide; 10 to 14 per cent. oxygen; about 80 per cent. nitrogen, and some water vapor. The ratio of oxygen to sulphur dioxide depends on whether the material burned is sulphur or pyrite. These hot gases pass through a flue into a dust chamber in which most of the dust is deposited. They then go to the Glover tower, passing upwards through the packing or filling of the tower, where they come in contact with a downward-flowing stream of weak sulphuric acid, and also the nitrous vitriol or the cold acid that has been used in the Gay-Lussac tower for recovery of the nitrogen oxides. Between the dust chamber and the Glover tower are usually placed the niter pots, which contain sodium nitrate and sulphuric acid and in which the necessary quantities of oxides of nitrogen are generated and added to the gases going to the Glover tower to maintain the proper amount of those oxides in the system.

43. The hot ascending gases evaporate a considerable portion of the water from the weak acid, thereby concentrating sulphuric acid and at the same time releasing the nitrous acid from the *nitrous vitriol*. The released oxide of nitrogen, the sulphur dioxide gas, and the water vapor pass over into the lead chambers where the reactions take place for the production of sulphuric acid. After leaving the chambers, the gases—consisting essentially of nitrogen, the excess oxygen, the oxides of nitrogen, and acid mist or water mist—are led through the Gay-Lussac towers, where the oxides of nitrogen are absorbed and recovered from the waste gases by strong sulphuric acid, forming nitrous vitriol. The waste gases are discharged from

the top of the Gay-Lussac tower either directly into the air or into a flue leading to a stack. As already indicated, the nitrous vitriol thus obtained is conducted to the Glover towers diluted with chamber acid, and the oxides of nitrogen are again liberated by heat and passed into the chamber system.

The acid produced in the chambers is dilute containing only about 60 to 65 per cent. H_2SO_4, and at many plants a large part or all of this chamber acid is passed through the Glover tower and concentrated to about 75 or 80 per cent. H_2SO_4.

44. Several theories have been advanced to explain the reactions occurring in the Glover towers and the lead chambers, and the part taken in these reactions by the nitrogen oxides. The theory most generally accepted is that of Lunge, which is a result of elaborate investigations made by him in 1884. According to this theory, sulphur dioxide (SO_2), nitrogen trioxide (N_2O_3), oxygen, and water vapor unite directly to form nitrosulphuric acid, the reaction being as follows:

$$2SO_2+N_2O_3+O_2+H_2O=2SO_2(OH)(ONO)$$

This complex substance floats around in the chamber as a mist until it meets water mist particles either as water or in the form of very dilute sulphuric acid; the nitrosulphuric acid is broken up into sulphuric acid and oxides of nitrogen, as follows:

$$2SO_2(OH)(ONO)+H_2O=2H_2SO_4+N_2O_3$$

45. Construction of Glover Towers.—Nearly all Glover towers have an outer shell of lead provided with an acid-proof stone, or brick lining, and packed with pure massive quartz or acid-proof brick or tile. In plants recently constructed the lead shell, which is part of the usual construction, has been eliminated and the towers are built entirely of chemical brick laid in acid-proof cement.

The size and shape of Glover towers vary greatly. There are circular, square, rectangular, and octagonal shaped towers varying in height from 15 to 60 feet and in area of external cross-section from 25 to 700 square feet.

46. Function of the Glover Tower.—The chief functions of the Glover tower are: (1) The denitration of the

nitrous vitriol; (2) the conversion into oxides of nitrogen of the nitric acid which is added to make up for the oxides of nitrogen lost in the process; (3) the concentration of weak chamber acid; (4) the cooling of the furnace gases; (5) production of acid in the upper part of the tower; (6) the cleaning of the furnace gases from impurities.

47. Construction of Gay-Lussac Towers.—Various styles of Gay-Lussac towers with different types of tower packing have been proposed. The most commonly used type is a lead tower much higher than it is wide, of circular or rectangular form and filled with a tower packing such as coke, quartz, or acid-proof stoneware. The packing is so arranged that the sulphuric-acid solution entering from above is broken into small drops or spray as it descends through the packing. The gases rise in numerous small streams through the interstices of the packing so that the surface of contact between acid and gas is as large as possible.

CONTACT PROCESS FOR MANUFACTURE OF SULPHURIC ACID

GENERAL DISCUSSION OF THE PROCESS

48. Contact Process.—A process that has been introduced successfully in the last few years is the catalytic, or contact, process. It is based on the fact that oxygen in the presence of platinized asbestos converts sulphur dioxide into sulphur trioxide:

$$2SO_2+O_2=2SO_3$$

which with water gives sulphuric acid:

$$SO_3+H_2O=H_2SO_4$$

49. Although the reaction between sulphur dioxide and oxygen is almost imperceptibly slow even at 400° C., in the absence of a catalyst, yet by the presence of certain catalysts the reaction is brought about quite rapidly. A catalyst does

not initiate a reaction, it merely affects the velocity with which the reaction occurs.

The various contact materials besides metallic platinum which have been tried as catalysts include oxides of iron, chromium, tin, bismuth, tungsten, titanium, molybdenum, thorium, and vanadium.

With the exception of ferric oxide, which has been used for one application of the contact process, none of these has proved to be successful. Ferric oxide, moreover, has not been as successfully used as platinum, which is the most effective contact substance now in use, and the contact-acid industry of the country is based on the use of that material in one form or another.

50. A mixture of sulphur dioxide and oxygen reacts energetically when first brought into contact with the heated platinum, but the reaction takes place more and more slowly as an increasing percentage of SO_3 is formed, and the final conversion of SO_2 into SO_3 is only attained by allowing the reacting gases to remain in contact with each other in the presence of the platinum for some considerable time. The higher the temperature the more rapidly is the final conversion attained, but as the reverse action ($SO_3 = SO_2 + O$) increases rapidly at the higher temperatures, the less favorable is the final result at these temperatures.

51. The essential facts and the conditions necessary for the successful operation of the contact process may be enumerated as follows:

1. When the sulphur dioxide (SO_2) gas mixed with a suitable proportion of oxygen is passed over heated platinum in a state of very fine subdivision, the reaction $2SO_2 + O_2 = 2SO_3$ takes place, forming sulphur trioxide or sulphuric acid anhydride (SO_3).

2. Sulphur trioxide is quantitatively absorbed by sulphuric acid solution of between 97.5 and 99.5 per cent. H_2SO_4 content, resulting in the uniting of the SO_3 with the excess water in the sulphuric acid solution and the consequent formation of stronger sulphuric acid (H_2SO_4).

3. The gases containing sulphur trioxide after leaving the converter should be cooled to a temperature of 50° or 60° C. or lower before entering the absorption installation. The sulphuric acid used for absorption is heated both by the sensible heat of the gases passing through it and by the heat of formation of the sulphuric acid formed by the uniting of the sulphur trioxide with the water in the acid solution. This acid must be continually cooled and preferably held down to a temperature of 40° C. or 50° C., as sulphur trioxide is not readily or completely absorbed in sulphuric acid solution when the temperature rises too high.

4. The strength of the absorbing acid must be very carefully maintained and should never vary more than 1 per cent. either way from a content of 98.5 per cent. H_2SO_4.

5. Oleum (fuming sulphuric acid) is manufactured by passing the cool gases containing SO_3 through strong sulphuric acid until the acid, through absorption and solution of SO_3, has reached the desired strength. This solution of sulphur trioxide in sulphuric acid to produce oleum also generates heat, and suitable cooling apparatus must be installed and operated in order to attain oleum of desired strength.

PHYSICAL AND CHEMICAL PROPERTIES OF SULPHURIC ACID

52. Physical Properties.—When sulphuric acid is pure and of 100 per cent. strength it is a heavy, colorless acid of oily consistency having a specific gravity of 1.83 at 18° C. When cooled it solidifies, the resulting crystals melting at 10.46° C. Pure sulphuric acid may be distilled but undergoes partial decomposition and loses more sulphur trioxide than water until an acid boiling at 338° C. and containing 98.3 per cent. of sulphuric acid is obtained.

Sulphuric acid possesses a very strong attraction for water. Thus it combines readily with the moisture of the air, and on account of the ease with which it absorbs water it is used largely in the laboratory and on a large scale as a drying agent for gases, the gas to be dried being caused to bubble through it.

53. Chemical Properties.—Sulphuric acid attacks most organic substances, removing the water from them, and completely charring or blackening them. When bodies have an excess of carbon that element is liberated. Thus concentrated sulphuric acid when mixed with a concentrated sugar solution causes the decomposition of the latter with the liberation of carbon. At a red heat the acid is decomposed into water, sulphur dioxide, and oxygen.

54. Salts of Sulphuric Acid.—Sulphuric acid, being dibasic, forms two kinds of salts; one normal, known as normal sulphate, but the other, still containing half of the hydrogen, is acid and is therefore called bisulphate.

The normal sulphates, which are neutral, are made by allowing sulphuric acid to act on sodium chloride at high temperatures, thus:

$$2NaCl+H_2SO_4=Na_2SO_4+2HCl$$

At lower temperatures the bisulphate is formed, thus:

$$NaCl+H_2SO_4=NaHSO_4+HCl$$

Normal sulphates may also be made as follows:

1. Passing SO_3 over the oxide of a metal at red heat,

$$SO_3+CaO=CaSO_4$$

2. By precipitation,

$$H_2SO_4+BaCl_2=BaSO_4+2HCl$$

3. By oxidation of sulphides,

$$CaS+2O_2=CaSO_4$$

55. Pyrosulphuric Acid.—Pyrosulphuric, disulphuric, or Nordhausen sulphuric acid, $H_2S_2O_7$, is another kind of sulphuric acid used in commerce. It may be regarded as a compound of a molecule of ordinary sulphuric acid with a molecule of sulphur trioxide:

$$H_2SO_4+SO_3=H_2S_2O_7$$

It is prepared by the distillation of partly dried ferrous sulphate in earthen retorts; upon heating ferrous sulphate, $FeSO_4 \cdot 7H_2O$, 6 molecules of water of crystallization are expelled, leaving $FeSO_4 \cdot H_2O$, and when this salt is more

strongly heated it breaks down into ferric oxide, Fe_2O_3, sulphur trioxide, SO_3, water, and sulphur dioxide, SO_2,

$$2FeSO_4 \cdot H_2O = Fe_2O_3 + SO_3 + SO_2 + 2H_2O$$

The above reaction, however, takes place in two stages which are represented by the following equations:

$$6FeSO_4 \cdot H_2O = \underset{\text{(ferric sulphate)}}{Fe_2(SO_4)_3} + 2Fe_2O_3 + 3SO_2 + 6H_2O$$

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$$

The sulphur trioxide set free is absorbed in strong sulphuric acid,

$$H_2SO_4 + SO_3 = H_2S_2O_7$$

Pyrosulphuric acid is used largely in the production of coal-tar dyes and colors. It is a heavy, oily liquid of specific gravity 1.9. It is usually more or less dark colored and hisses like a hot iron when dropped into water; it fumes strongly when exposed to air and is consequently very often called fuming sulphuric acid. It is now manufactured on a large scale by conducting sulphur trioxide, made by passing sulphur dioxide and oxygen over platinized asbestos at a high temperature, through ordinary sulphuric acid (contact process). It is sometimes called solid sulphuric acid because it solidifies when cooled, forming crystals that melt at 35° C.

NOMENCLATURE OF SULPHURIC ACID

56. As the specific gravity of sulphuric acid can be determined more easily than the strength, acid weaker than 93.19 per cent. H_2SO_4 is nearly always spoken of and sold as being of so many degrees Baumé, the Baumé hydrometer being the instrument generally used for determining the specific gravity. The following is a list of the principal commercial strengths of acid showing the values in Baumé degrees and their H_2SO_4 equivalent as formulated by the Manufacturing Chemists' Association in 1882:

Degrees Baumé	Per Cent. H_2SO_4
50	62.18
60	77.67
66 (oil of vitriol)	93.19

Acids between 93.19 per cent. H_2SO_4 and 100 per cent. H_2SO_4 are spoken of as so many per cent. sulphuric acid, 100 per cent. being commonly called monohydrate.

57. SO_3 dissolves in the monohydrate giving fuming acid or *oleum*. There are three ways of stating the strength of fuming acid: (1) The percentage of free (dissolved) SO_3; (2) the percentage of total SO_3; (3) the equivalent percentage of 100 per cent. H_2SO_4; that is, the percentage of 100 per cent. H_2SO_4 the fuming acid would make if sufficient water were added to combine with all the free SO_3. For example: Twenty per cent. oleum would contain 20 per cent. free SO_3 and 80 per cent. actual H_2SO_4, or would contain 85.28 per cent. SO_3, thus: Sulphuric acid contains $\overset{98}{H_2SO_4}$———$\overset{80}{SO_3}$; $\frac{80\times100}{98}=81.6$ per cent. SO_3 and 81.6 per cent. $\times80$ per cent. $=65.28$ per cent. and 65.28 per cent. $+20$ per cent. $=85.28$ per cent. total SO_3. If sufficient water were added to combine with all the free SO_3 the oleum would make 104.5 per cent. of H_2SO_4. Thus:

$$\overset{80}{SO_3}+\overset{18}{H_2O}=\overset{98}{H_2SO_4}$$

$$98\div80=1.225$$

1.225×20 per cent. $\times100=24.5$ per cent. and 24.5 per cent. $+80=104.5$ per cent. H_2SO_4.

The following conversion factors are given for convenience:

1. Fifty-degree B. acid (chamber acid) contains 50.76 per cent. SO_3 or 62.18 per cent. H_2SO_4. A stated weight of 50° B. acid multiplied by 0.8 ($62.18\div77.67=.8$) gives the equivalent weight of 60° acid, or multiplied by the fraction $\frac{2}{3}$, $\left(\frac{62.18}{93.19}=\frac{2}{3}\right.$, approximately$\left.\right)$ gives the equivalent weight of 66° acid.

2. Sixty-degree B. acid contains 63.41 per cent. SO_3 or 77.67 per cent. H_2SO_4. A stated weight of 60° acid multiplied by 1.25 ($77.67\div62.18=1.25$) gives the equivalent weight of 50° acid, or, multiplied by the fraction $\frac{5}{6}$, $\left(\frac{77.67}{93.19}=\frac{5}{6}\right)$ gives the equivalent weight of 66° acid.

3. Sixty-six degree B. acid (oil of vitriol) contains 76 per cent. SO_3 or 93.19 per cent. H_2SO_4. A stated weight of 66° acid multiplied by 1.2 ($93.19 \div 77.67 = 1.2$) gives the equivalent weight of 60° acid, and multiplied by 1.5 ($93.19 \div 62.18 = 1.5$) gives the equivalent weight of 50° acid.

USES OF SULPHURIC ACID

58. Sulphuric acid is used in the chemical and metallurgical industries of this country in so many ways that the compilation of a complete list of its uses would be a difficult task. Therefore, only the more important uses are given in the following résumé:

1. Dilute acid—that is, 60° B. (77.67 per cent. H_2SO_4) acid, or weaker—is used in the manufacture of fertilizers, ammonium sulphate, and sulphates of metals (magnesium, aluminum, iron, zinc, copper); in precipitating barium and calcium sulphate for chemical purposes; in the manufacture of mineral acids (nitric, hydrochloric, boric, carbonic, and chromic) and various organic acids (oxalic, tartaric, citric, acetic, and stearic); in pickling sheet iron for tinning and galvanizing; in various metallurgical operations; in the production of copper, zinc, nickel, silver, and gold; for various types of galvanic batteries, storage batteries, electroplating; in the manufacture of ether; in making and purifying many organic coloring matters; in making starch, sirup, and sugar; and in innumerable other chemical and industrial operations.

2. Concentrated acid—that is, acid 60° B. (77.67 per cent. H_2SO_4) to the 100 per cent. H_2SO_4 made by the contact process—is used for purifying benzene, petroleum, paraffin oil, and other mineral oils; for manufacture of nitroglycerine, pyroxylin, nitrobenzene, picric acid, and various other nitro compounds and nitro ethers; and in the manufacture of the fatty acids by distillation.

3. Fuming acid (oleum), also made by the contact process, is used for the manufacture of various forms of explosives, as nitrocellulose, trinitrotoluol, picric acid, and nitroglycerine, and for fortifying weaker acids.

Of all the uses, the following take the greatest tonnage of acid: (1) Manufacture of phosphate fertilizer; (2) refining of petroleum products; (3) pickling of iron and steel; (4) manufacture of nitrocellulose, nitroglycerine, celluloid, etc.; (5) general chemical and metallurgical operations.

THE POLYTHIONIC SERIES

59. All of the oxygen acids of sulphur, with the exception of pyrosulphuric acid, heretofore described, contain only 1 atom of sulphur. Another series of acids exists, however, called the polythionic series, in which each member contains a variable number of sulphur atoms. The names of these acids and their sodium salts follow.

Name of Acid	Formula	Name of Salt	Formula
Thiosulphuric acid	$H_2S_2O_3$	Sodium thiosulphate	$Na_2S_2O_3$
Dithionic acid	$H_2S_2O_6$	Sodium dithionate	$Na_2S_2O_6$
Trithionic acid	$H_2S_3O_6$	Sodium trithionate	$Na_2S_3O_6$
Tetrathionic acid	$H_2S_4O_6$	Sodium tetrathionate	$Na_2S_4O_6$
Pentathionic acid	$H_2S_5O_6$	Sodium pentathionate	$Na_2S_5O_6$

The acids of this series, likewise their salts, are unstable, the former decomposing into sulphuric acid, sulphur dioxide, and free sulphur when the attempt is made to concentrate their aqueous solutions.

60. Thiosulphuric Acid.—By far the most important member of the polythionic series is thiosulphuric acid. This compound is known only in its water solution, but its salts, especially *sodium thiosulphate*, are in common use. Sodium thiosulphate is formed when a solution of sodium sulphite is boiled with sulphur; thus:

$$Na_2SO_3 + S = Na_2S_2O_3$$

This salt is commonly called sodium hyposulphite or *hypo*. It is used to a great extent in chemical analysis, in photography, and for the purpose of removing chlorine from fabrics which have been bleached.

SULPHUR AND CHLORINE

61. Compounds of Sulphur and Chlorine.—Three compounds of sulphur and chlorine, (*a*) sulphur monochloride, S_2Cl_2, (*b*) sulphur dichloride, SCl_2, (*c*) sulphur tetrachloride, SCl_4, are formed by the direct union of their constituents. The first is formed when the sulphur is present in excess, the last when the chlorine is most abundant.

(*a*) Sulphur monochloride, S_2Cl_2, the most stable of the chlorides of sulphur, is an active, reddish-yellow liquid, specific gravity 1.709, possessing a peculiar, penetrating, disagreeable odor, fuming strongly in the air, and boiling at 138° C. It is decomposed by metals, liberating sulphur and forming the chloride of the metal. Sulphur readily dissolves in the monochloride, forming a thick liquid containing 66 per cent. of sulphur.

Sulphur monochloride is used extensively in the rubber industries as a vulcanizing agent.

(*b*) Sulphur dichloride, SCl_2, is prepared by passing chlorine to saturation into sulphur monochloride cooled by a mixture of ice and salt, and expelling the excess of chlorine by a stream of carbon dioxide. The compound thus obtained is a dark-red liquid boiling at 64° C., and having a specific gravity of 1.62. It decomposes even at ordinary temperatures into the monochloride and chlorine.

(*c*) Sulphur tetrachloride, SCl_4, is prepared by saturating sulphur monochloride with chlorine at a temperature of −22° C. It is a yellowish-brown mobile liquid which only exists at temperatures below 0° C. When removed from a freezing mixture it immediately begins to dissociate with the evolution of chlorine.

62. Sulphuryl Chloride.—When sulphur dioxide and chlorine are brought together in the presence of sunlight and a little camphor, the latter acting as a catalytic agent, a colorless liquid, sulphuryl chloride, SO_2Cl_2, is obtained, which boils at 69° C. When treated with water, sulphuryl chloride decomposes with the formation of sulphuric and hydrochloric acids.

$$SO_2Cl_2+2H_2O=H_2SO_4+2HCl$$

63. Chlorosulphonic Acid. — Chlorosulphonic acid, $SO_2Cl(OH)$, may be prepared by the interaction of sulphur trioxide and hydrogen chloride,

$$SO_3+HCl=SO_2Cl(OH)$$

It is a heavy, colorless, fuming liquid boiling at 155° C. When brought in contact with water it reacts with explosive violence, hydrochloric and sulphuric acids being formed:

$$SO_2Cl(OH)+H_2O=HCl+H_2SO_4$$

SELENIUM

Symbol Se. Atomic weight 79.2. Molecular weight 158.4.

64. History.—The rare element selenium was discovered by Berzelius in the year 1817. The name, derived from the Greek word *selene*, meaning moon, was given the element because of its close resemblance to the element tellurium (the earth). It is also closely related to sulphur in its physical characteristics and chemical relations to other bodies.

65. Occurrence.—Although selenium is somewhat widely distributed, it occurs only in small quantities. It occurs together with sulphur in Hawaii and in combination with minerals in Sweden, Argentine Republic, the Hartz Mountains, and in Mexico. It also occurs in small quantities with sulphides of iron, copper, and zinc, but never native. Some iron pyrites contain selenium and when these are roasted in the preparation of sulphuric acid selenium settles out in chimney dust. It also occurs with tellurium in the flue dust obtained from some ores of gold and silver.

66. Preparation.—Selenium is prepared from the red deposit found in the flue dust of sulphuric-acid works by washing the scale with water and digesting with a potassium cyanide solution at 80° C. until the red color entirely disappears, potassium selenocyanide, $KSeCN$, being formed. The solution is then filtered and hydrochloric acid added to the filtrate, selenium being precipitated; thus:

$$KSeCN + HCl = KCl + HCN + Se$$

The product is then purified by oxidation, thus

$$Se + O_2 = SeO_2$$

the oxide being sublimed and reduced to the metal by means of sulphur dioxide, thus:

$$SeO_2 + H_2O = H_2SeO_3 \text{ (selenous acid)}$$
$$H_2SeO_3 + H_2O + 2SO_2 = 2H_2SO_4 + Se$$

67. Properties.—Like sulphur, selenium exists in various allotropic modifications, three of which are known; namely, amorphous, crystalline, and metallic selenium. The first two are soluble in carbon disulphide, but the latter is not.

The amorphous modification is obtained as a brick-red powder when selenous acid is reduced in the cold by sulphur dioxide. It is also obtained when either iron, zinc, or stannous chloride is used for the reduction, and also by the electrolysis of the acid. It has a specific gravity of 4.26 and is soluble in carbon disulphide. When a solution of amorphous selenium in carbon disulphide is poured into a large volume of ether it separates in a colloidal form, soluble in water, forming a red fluorescent solution that may be boiled without change. If the solution of amorphous selenium is heated to 217° C. and then rapidly cooled, vitreous selenium is formed. This solidifies as a brownish-black translucent mass and is very brittle.

68. The crystalline modification is obtained when amorphous selenium is heated to 100° C. Its temperature suddenly rises to 217° C. in the act of crystallization. It is a dark-gray crystalline mass, crystallizing in prismatic crystals. It has a specific gravity of 4.5, and is soluble in carbon disulphide.

Metallic selenium is obtained by gradually heating the amorphous modification or by cooling melted amorphous selenium quickly to 210° C. and keeping the mass at this temperature for some time. It has a specific gravity of 4.8, is insoluble in carbon disulphide, melts at 217° C., and boils at 690° C. It conducts electricity and exposure to light increases its conductivity. Selenium burns in the air with a bright-blue flame emitting an odor of rotten horseradish.

COMPOUNDS OF SELENIUM

69. Selenium Dioxide.—Selenium dioxide, SeO_2, is the oxide of selenium known with certainty to exist in the free state. Berzelius states that the peculiar odor given off by selenium when burned in the air is due to the formation of a lower oxide, but this oxide has never been isolated. The dioxide is obtained when selenium is strongly heated in a stream of oxygen, in the form of long white needles, which sublime without fusion at 320° C. It is readily soluble in boiling water, forming selenous acid, H_2SeO_3,

$$SeO_2+H_2O=H_2SeO_3$$

70. Selenic Acid.—Selenic acid, H_2SeO_4. is prepared by the action of chlorine on selenium in the presence of water, thus:

$$Se+3Cl_2+4H_2O=H_2SeO_4+6HCl$$

Selenous acid and the selenites are converted in selenic acid and selenates in the same manner. By fusing selenium with potassium nitrate, the potassium salt of selenic acid is obtained, thus·

$$Se+2KNO_3=K_2SeO_4+2NO$$

When subjected to concentration until a specific gravity of 2.6 is obtained, selenic acid becomes a colorless, very acid, oily liquid miscible with water in all proportions with the evolution of heat. The hot acid dissolves gold and copper. Iron, zinc, and other metals dissolve in it, forming selenates with the evolution of hydrogen. Concentrated hydrochloric acid, when boiled with selenic acid, decomposes it with the formation of selenous acid and chlorine. This mixture will dissolve gold and platinum, owing to the chlorine set free. Sulphur dioxide and hydrogen sulphide do not reduce selenic acid, in which respect this acid differs from selenous acid.

Evaporated in a vacuum at 180° C. and then cooled, selenic acid crystallizes in long, hexagonal prisms of the pure acid. These melt at 58° C., have a specific gravity of 2.95, and combine readily with water, forming a monohydrate melting at 25° C.

71. Hydrogen Selenide.—Hydrogen selenide, H_2Se, also known as hydroselenic acid, is prepared by treating ferrous selenide, $FeSe$, with concentrated hydrochloric acid.

The ferrous selenide is first made by heating selenium with iron filings,

$$Se+Fe=FeSe$$
$$FeSe+2HCl=H_2Se+FeCl_2$$

Hydrogen selenide is also formed by heating the vapor of selenium with hydrogen at 250° C. to 600° C.:

$$Se+H_2=H_2Se$$

It is a colorless gas possessing an odor which at first resembles hydrogen sulphide but later becomes more offensive. It is inflammable and very poisonous. Exposed to light, hydrogen selenide decomposes into its elements. It can be condensed to a liquid. It solidifies at −64° C., boils at −42° C., and has a specific gravity of 2.1. Hydrogen selenide is soluble in water, reddens blue litmus paper, and colors the skin a reddish brown. The aqueous solution on exposure to the air decomposes with the separation of red selenium. It produces precipitates of the selenides of the heavy metals, as does hydrogen sulphide.

72. Halogen Compounds of Selenium.—Selenium forms the following compounds with the halogens: Tetrafluoride, SeF_4; tetrabromide, $SeBr_4$; hexafluoride, SeF_6; monoiodide, Se_2I_2; monochloride, Se_2Cl_2; tetraiodide, SeI_4; tetrachloride, $SeCl_4$; chlorobromides, $SeCl_3Br$, $SeClBr_3$; monobromide, Se_2Br_2. The tetrafluoride is a colorless fuming liquid boiling at a little over 100° C., and the hexafluoride is a white crystalline mass at −78° C., and soon becomes gaseous when the temperature is raised. The monochloride exists as a brown, oily liquid that cannot be distilled without decomposition. Selenium tetrachloride is a light-yellow solid, volatilizes readily, and sublimes in small crystals. The monobromide forms a black, almost opaque, liquid with a disagreeable odor. Acted on by bromine, it changes to the tetrabromide. This is an orange-yellow crystalline mass, is volatile, vaporizing between 75° C. and 80° C., with slight decomposition, recrystallizing in black six-sided scales. It has a peculiar disagreeable odor and

decomposes in moist air. The mono- and tetra-iodides are both crystalline. The former crystallizes in a black shining mass that melts at 70° C., and the latter forms dark granular crystals that melt at 80° C. to a brownish-black liquid. The chloro-bromides both form orange-yellow crystalline substances.

73. Uses for Selenium and Its Compounds.—Up to the present time very little practical use has been made of selenium and it is estimated that a production of a few hundred pounds annually would supply the demand. During the recent war, owing to the scarcity of manganese, selenium was used in the manufacture of glass to destroy the green color due to iron.

As previously mentioned, the electrical conductivity of metallic selenium increases when it is exposed to light. This property has been made use of in the development of the selenium cell, which is used in wireless telephony and as a means of automatically turning down or extinguishing gas lights and buoy lights at daybreak.

74. Some research work has been done with the object in view of using selenium compounds as substitutes for sulphur compounds or even as a possibility of improving the quality of rubber compounds, dyes, etc. in which sulphur compounds have heretofore been used. Selenium, however, is a much more expensive material than sulphur and it is evident that up to the present time any improvement resulting from its use in certain lines of manufacture has not been sufficiently great to warrant its use to the exclusion of sulphur.

Quite recently, results obtained in developing the use of selenium oxychloride, $SeOCl_2$, as a solvent have been published, but whether or not the advantages claimed for this compound will cause it to come into general use, remains to be seen.

TELLURIUM

Symbol Te. Atomic weight 127.5.

75. History and Occurrence.—Tellurium occurs in small quantities in a few places in Germany, Mexico, United States, Brazil, Bolivia, and Australia. It also occurs native. In 1798 Klaproth made an investigation of the tellurium ores and named the metal tellurium, from *tellus*, the earth. From exhaustive investigations of tellurium and its compounds it was decided that the substance itself was a metal. Its compounds, however, were found to resemble so closely those of sulphur and selenium that it was placed in the sulphur group. It is usually found in combination with other metals, as with gold and silver in sylvanite, $(AgAu)Te_2$; with silver as hessite, Ag_2Te; with bismuth as tetradymite, Bi_2Te_3; etc.

76. Preparation.—Pure tellurium is prepared from tetradymite (bismuth telluride, Bi_2Te_3), which is mixed with an equal quantity of pure sodium carbonate, the mixture made into a thick paste with oil, which supplies the carbon necessary for the reduction, and heated strongly in a tightly closed crucible. If pure bismuth telluride were subjected to this treatment, the final products of the reaction would probably be represented as follows:

$$Bi_2Te_3+3Na_2CO_3+C=3Na_2Te+Bi_2O_5+4CO$$

The fusion mixture is then leached with air-free water, to prevent oxidation of the sodium telluride at this stage in the process, and the solution filtered. Compressed air is then passed through this filtered solution, the sodium telluride being oxidized and tellurium oxide precipitated in the form of a gray powder,

$$Na_2Te+O_2+H_2O=2NaOH+TeO$$

This is reduced by distillation in a stream of hydrogen,

$$TeO+H_2=Te+H_2O$$

Occurring as it does in combination with gold and silver, it is found condensed in the fume chambers of gold and silver smelters in the form of dust. This dust is digested with

sodium carbonate and potassium cyanide solution, the resulting solution decanted, then acidified with nitric acid, and the tellurium precipitated by hydrogen sulphide.

77. Crude tellurium is best purified by dissolving in aqua regia (nitro-hydrochloric acid). The excess of nitric acid is expelled by evaporation with an excess of hydrochloric acid. The concentrated liquid is then diluted to keep the tellurous acid in solution and to precipitate the lead chloride. The lead chloride is removed by filtering and the tellurium precipitated by sulphurous acid. The tellurium thus obtained is then distilled in a current of hydrogen.

78. Properties.—Tellurium is a silver-white, brittle, crystalline solid with a strong metallic luster and a specific gravity of 6.24. It conducts heat and electricity readily and crystallizes in rhombohedrons. It melts at 452° C., volatilizes at 1,390° C., and can be distilled. Its vapor is greenish-yellow, resembling that of chlorine. When heated in the air it takes fire and burns with a blue flame tinged with green, evolving white fumes of tellurous oxide. In all its physical properties, tellurium closely resembles a metal, but, being so closely allied chemically to sulphur and selenium, it is justifiable to regard it as a non-metal and consider it with these elements. Its binary compounds are known as tellurides. It forms two chlorides, $TeCl_2$ and $TeCl_4$, and two bromides, $TeBr_2$ and $TeBr_4$.

As in the case of selenium, very few uses have been developed for tellurium or its compounds.

REVIEW OF THE OXYGEN-SULPHUR GROUP

79. The same gradation of properties that has been noticed in the halogen group may also be noticed between the elements oxygen, sulphur, selenium, and tellurium, although the relationship is not so clearly defined as in the case of the halogens. All of the elements of the oxygen-sulphur group exhibit a valence of 2 in the majority of their compounds and all exist in different allotropic modifications. Again, they all unite with hydrogen to form compounds of the same general type.

Thus, we have H_2O, H_2S, H_2Se, and H_2Te. The latter three compounds are gases possessing strong characteristic odors, while the first named compound is an odorless, colorless, and, when pure, a tasteless liquid.

80. As in the case of hydrogen, many similar oxygen compounds are formed by the metals of this group. In this connection, however, it must be remembered that, while oxygen and sulphur and their compounds have been rather thoroughly

TABLE I

COMPARISON OF PROPERTIES

Property	Oxygen	Sulphur	Selenium	Tellurium
Atomic weight...	16	32.06	79.2	127.5
Specific gravity*.	1.43	1.92–2.07	4.26–4.80	6.015–6.27
Melting point...	$-227°$	114°–120°	170°–217°	446°–452°
Boiling point....	$-182.7°$	444.6°	690°	1,390°

*Of the solid.

investigated, the compounds of selenium and tellurium have not been. The compounds, SO_2, SeO_2, and TeO_2, are, however, known to exist. The general chemical activity of the elements of this group decreases with the increase in atomic weight, the stability of their halogen compounds increases with the increase in atomic weight. Thus, OCl_2 is very unstable, SCl_2 and SCl_4 exist only at low temperatures, but $SeCl_4$, $TeCl_2$, and $TeCl_4$ even exist as gases. Table I gives a comparison of the properties of the oxygen-sulphur group.

INORGANIC CHEMISTRY
(PART 8)

NITROGEN-PHOSPHORUS GROUP

GENERAL REMARKS

1. The group of elements to be studied in this Section consists of the elements nitrogen, phosphorus, arsenic, antimony, and bismuth. The element nitrogen, the properties of which have already been studied, bears the same relation to the other members of this group that fluorine bears to the members of the halogen group, and that oxygen bears to the oxygen-sulphur group. That is, the relationship between nitrogen and the other members of the group is not so close as is the relationship existing between the other four members of the group. Speaking broadly, it may be said that all the members of the group form compounds of a similar character and composition. There is, however, a gradual gradation of properties from nitrogen to bismuth. While as a whole the members of this group are acid formers, this property is less marked as we pass toward the heavier elements. Thus, nitrogen forms strong acids; phosphorus and arsenic, less strong; antimony, almost as many basic as acid compounds; bismuth more basic than acid. The hydrogen compounds of these elements grow less stable from nitrogen to antimony, and bismuth will not form a compound with it. The hydrogen compounds are: NH_3, PH_3, AsH_3, and SbH_3. The first one, NH_3, is strongly basic; the corresponding compound of phosphorus is weakly basic,

while the hydrogen compounds of arsenic and antimony have no basic properties. Thus it is seen that in this group, as in the other groups that have been studied, there is a gradual gradation of properties from the light to the heavy elements.

PHOSPHORUS

Symbol P. Atomic weight 31.04. Molecular formula, P_4. *Molecular weight 124.16.*

2. History and Occurrence.—Phosphorus was first obtained by Brand of Hamburg in 1669 by heating strongly a mixture of evaporated urine and sand in an earthen retort. In 1771 Scheele found it could also be made from bones. Phosphorus derives its name from a Greek word meaning *light bearer,* from its property of glowing in the dark. Owing to its great affinity for oxygen, it is never found free in nature. It is, however, very widely distributed and is found abundantly in the form of calcium phosphate, $Ca_3(PO_4)_2$. The minerals containing phosphates are subject to disintegration and thus phosphorus is caused to pass into the soil from which it is extracted by plants. No plants will grow in a soil destitute of phosphorus, as it is required to build up certain parts of plant structure, particularly the fruit and seeds. As animals feed on plants, the phosphorus enters the bodies, where it is found particularly in the bones, which contain about three-fifths of their weight of calcium phosphate.

3. Preparation.—Phosphorus is the only element for the ordinary preparation of which animal substances are employed. It is prepared by treating burned bones with sulphuric acid, acid calcium phosphate being formed; thus,

$$\underset{\text{calcium phosphate}}{Ca_3(PO_4)_2}+\underset{\text{sulphuric acid}}{2H_2SO_4}=\underset{\text{calcium sulphate}}{2CaSO_4}+\underset{\text{acid calcium phosphate}}{H_4Ca(PO_4)_2}$$

The mass is then digested in water which dissolves the acid calcium phosphate, the resulting solution being then drawn off, evaporated, and the residue strongly heated with charcoal.

Upon evaporating the solution of acid calcium phosphate to dryness, this compound loses 2 molecules of water and is converted into calcium metaphosphate, $Ca(PO_3)_2$, thus:

$$H_4Ca(PO_4)_2 = Ca(PO_3)_2 + 2H_2O$$

and the calcium metaphosphate heated with charcoal forms phosphorus and calcium phosphate, $Ca_3(PO_4)_2$,

$$3Ca(PO_3)_2 + 10C = Ca_3(PO_4)_2 + P_4 + 10CO$$

4. Commercial Manufacture of Phosphorus.—In the manufacture of phosphorus on a large scale the organic material in the bones is used in several ways. In order to extract the gelatin the bones are boiled with water, or treated with superheated steam. Sometimes they are heated in iron

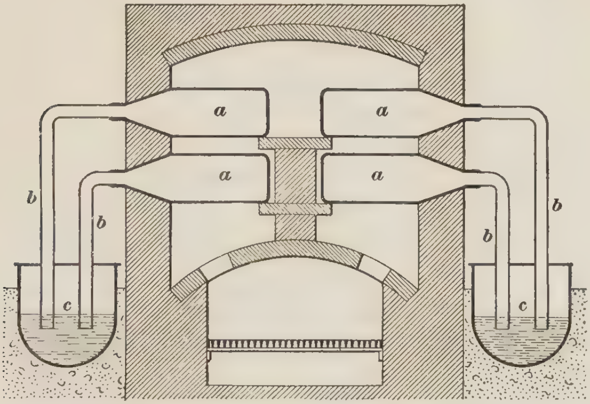


Fig. 1

retorts to distil off ammonia and other volatile substances. If the latter procedure is followed, the residue after the distillation consists of bone black, bone coal, or animal charcoal, which is used in the manufacture of sugar, syrups, and various other articles. After the animal charcoal has become useless for these purposes, it is completely burned in an open fire and converted into bone ash. To prepare phosphorus, the bone ash is mixed with two-thirds of its weight of strong sulphuric acid diluted with 18 to 20 parts of water, well stirred, and allowed to stand for about 12 to 14 hours. The clear liquid is decanted

from the sediment, which consists of calcium sulphate; it is then evaporated in a pan to a syrupy consistence, mixed with one-fifth of its weight of charcoal, finely powdered, and heated to redness. The mixture is now distilled in bottle-shaped fire-clay retorts 3 feet long. The arrangement of these retorts in the distilling furnace is shown in Fig. 1. As a rule, each furnace has twenty-four retorts placed in two rows, one above the other. The temperature in the retorts *a* is raised to a bright red heat before they are charged with the mixture; the temperature is then increased to a white heat, which causes the phosphorus to distil over. The mouths of the retorts are connected to the pipes *b* which dip into troughs *c* containing water. These troughs run along the whole length of the furnace and in them the phosphorus condenses. The crude phosphorus is melted under hot water and thoroughly stirred, the greater proportion of the coarse suspended matter rising to the surface. Theoretically, the bone ash should yield about 11 per cent. of phosphorus, but practically hardly more than from 8 per cent. to 9 per cent. is obtained.

The crude phosphorus is purified by enclosing it in a chamois-skin sack, and strongly compressing it under water at 50° C.; the phosphorus passes through the leather and collects under the water. It is molded into sticks by being drawn into slightly conical glass tubes, which are then plunged into cold water. The phosphorus solidifies and is easily drawn from the tubes.

5. Phosphorus is prepared also by an electrical process known as the Readman, Parker, and Robinson system, in which the calcium phosphate is converted directly into phosphorus without previous treatment with sulphuric acid. The phosphate is mixed with charcoal and other fluxes, heated to as high a temperature as possible, and then introduced into an electrical furnace, which consists of an iron tank lined with refractory material, and contains large carbon electrodes in the sides. At the high temperature attained phosphorus vapor mixed with other gases passes over and is condensed. The slag formed is drawn off at intervals and fresh material charged into the furnace, the process in this way being made continuous.

6. Physical Properties.—Two varieties of phosphorus are known to exist, viz.: the yellow and the red. When first prepared away from light, ordinary, or yellow, phosphorus is an almost colorless, transparent solid having a specific gravity of 1.83. When exposed to light, however, its surface becomes coated with an opaque white film which soon changes to yellow, brown, and then red, and if exposed for a sufficiently long time the mass becomes red throughout.

At ordinary temperatures, yellow phosphorus has the consistency of beeswax and may be easily cut with a knife. At the freezing point of water, however, it becomes rather brittle and shows, when broken, evidences of crystalline structure. It melts at 44.1° C. and boils at 290° C. It is slightly volatile at ordinary temperatures. When exposed to the air, which always contains some water vapor, white poisonous fumes are evolved possessing a garlic-like odor. In the dark in contact with moist air phosphorus emits a pale white light. Traces of naphtha or oil of turpentine destroy its luminous properties.

In match factories where large quantities of this variety of phosphorus are used, the workers frequently suffer from a disease that attacks the teeth and jawbones and especially where the worker is exposed to phosphorus vapors.

Phosphorus is only slightly soluble in water, but dissolves readily in carbon disulphide, in phosphorus chloride, slightly in alcohol, and in ether, and in certain volatile oils. It is characterized by its great inflammability; at a temperature a little over its melting point it takes fire, and burns brightly with the formation of phosphorus pentoxide. Phosphorus is easily ignited by slight friction.

Owing to the readiness with which it undergoes oxidation, phosphorus is always kept under water, which it does not decompose.

7. When yellow phosphorus is heated to a temperature of from 240° to 250° C. in a vessel from which air is excluded, red phosphorus is formed. This modification of the yellow variety exists as a dark-red powder, tasteless and non-poisonous, consisting of small flat crystals, having a specific gravity

of 2.296. It has no odor, is not luminous when exposed to air, does not oxidize, and, consequently, need not be preserved under water. It remains solid up to a temperature beyond 250° C., and does not take fire when heated in the air until 260° C. is reached. At about this point it changes into the yellow variety and burns.

If the heating is conducted in a retort filled with carbon dioxide, so as to prevent combustion, the same weight of yellow phosphorus is produced, which proves most convincingly that the two varieties are only allotropic modifications of one and the same element. Further, both when burned produce the same weight of phosphorus pentoxide, P_2O_5.

The change from the yellow to the red variety is much accelerated by the presence of iodine in small quantities.

8. Chemical Properties of Yellow Phosphorus. Phosphorus does not unite with pure dry oxygen at tempera-

TABLE I

PROPERTIES OF YELLOW AND RED PHOSPHORUS

Properties	Yellow Phosphorus	Red Phosphorus
Color	Faint yellow	Red-violet
Smell	Garlic	Odorless
Exposure to air	Phosphorescence	No phosphorescence
Melting point	44.1° C.	725° C.
Physiological effects	Poisonous	Non-poisonous
Specific gravity	1.831	2.296
Solubility in carbon bisulphide	Soluble	Insoluble
Inflammability with chlorine	Ignites spontaneously	Ignites spontaneously

tures below 27° C., but if the oxygen be slightly diluted with nitrogen, oxidation takes place. If traces of the vapors of ethylene, turpentine, or ether are introduced into the air surrounding glowing phosphorus, phosphorescence is immediately destroyed. Chemically, yellow phosphorus is an active element; it unites vigorously with oxygen and the halogens and with sulphur and the metals at high temperatures.

9. Chemical Properties of Red Phosphorus. Chemically, red phosphorus is not as active as the yellow variety. Heated at 260° C. in air, it ignites, phosphorus pentoxide, P_2O_5, being formed. Red phosphorus will burn if heated in an atmosphere of chlorine, but no heat is necessary to cause yellow phosphorus to combine with chlorine. A summary of the properties of yellow and of red phosphorus will be found in Table I.

10. Uses of Phosphorus.—The greater part of the phosphorus produced is used in the manufacture of matches, but a small quantity is used in the manufacture of alloys such as phosphor-bronze, in the manufacture of rat poisons, and in medicine.

11. Matches.—The first matches were made about the year 1827. Up to this time fire had been artificially obtained by tinder and flint. The first matches were made of pieces of wood, the ends of which had been dipped into sulphur and coated with a mixture of sugar and potassium chlorate. These matches were ignited by being dipped into a bottle containing asbestos moistened with fuming sulphuric acid. Later the sulphured ends of the matches were dipped in a mixture of antimony sulphide and potassium chlorate made into a paste with gum. These were ignited by drawing between two pieces of sandpaper. Phosphorus soon replaced the sulphide of antimony, and potassium nitrate was substituted for the chlorate, thus overcoming the danger of an explosive ignition. Another improvement was the substitution of wax for sulphur, overcoming in this way the disagreeable odor due to the burning sulphur.

The discovery of red phosphorus and its non-poisonous character led to the use of this substance in the manufacture of matches. This substance has been found very valuable, as its use overcomes the phosphorus disease caused by the use of the white phosphorus. In fact at this time it is unlawful to use white phosphorus in the manufacture of matches.

The Swedish, or safety, matches are tipped with a mixture of potassium chlorate, potassium bichromate, red lead, and sul-

phide of antimony. This mixture will not ignite by simple friction, but will ignite when rubbed upon a mixture of red phosphorus and finely ground glass spread on the sides of the box.

PHOSPHORUS AND HYDROGEN

12. Compounds of Phosphorus and Hydrogen. Three compounds of phosphorus and hydrogen, called hydrogen phosphides, or phosphorus hydrides, are known. They are: Phosphine, PH_3, a gaseous compound; a liquid hydride, P_2H_4, and a solid hydride, P_4H_2.

13. Phosphine.—Phosphine, PH_3, may be made by boiling yellow phosphorus with a strong solution of sodium or

Fig. 2

potassium hydroxide, as follows: Fit up a retort with a delivery tube, with its end leading into a pneumatic trough, as shown in Fig. 2, and arrange the whole in a retort stand. Introduce into the retort a few fragments of potassium hydroxide together with some small pieces of phosphorus and a little water. Pass carbon dioxide through the tubulure so as to

displace the air completely; then close the tubulure tightly. Gently heat the retort; bubbles of gas soon rise and displace the carbon dioxide. In a short time, each bubble, as it rises to the surface of the water in the pneumatic trough bursts into flame and generates an extremely beautiful ring of white smoke which rotates on its circular axis as it ascends. If the air of the room is still, several of these rings will follow one another up to the ceiling.

The reaction by which phosphine is thus produced is a somewhat complicated one but may be expressed thus:

$$\underset{\text{phosphorus}}{P_4} + \underset{\substack{\text{potassium}\\\text{hydroxide}}}{3KOH} + \underset{\text{water}}{3H_2O} = \underset{\substack{\text{potassium}\\\text{hypophosphite}}}{3KH_2PO_2} + \underset{\text{phosphine}}{PH_3}$$

In addition to phosphine, PH_3, traces of P_2H_4 are formed, which cause the gas to inflame spontaneously. If the gas is collected in a jar, on standing it loses this property of spontaneous inflammability because the second phosphide, P_2H_4, suffers decomposition. In this method of preparing the gas, milk of lime (that is, calcium hydroxide suspended in water) may be employed instead of potassium hydroxide.

Phosphine may also be prepared by treating *calcium phosphide* with water,

$$Ca_3P_2+6H_2O=3Ca(OH)_2+2PH_3$$

and by decomposing phosphonium iodide, PH_4I, by means of potassium hydroxide.

$$PH_4I+KOH=PH_3+KI+H_2O$$

14. Properties of Phosphine.—Phosphine is a colorless gas with an unpleasant odor of putrid fish. It is sparingly soluble in water, is condensable to a liquid at $-85°$ C., and is neutral in its reactions. It takes fire readily at 100° C., burning with a brilliant flame, but is not a supporter of combustion. The aqueous solution of phosphine decomposes in the light into hydrogen and red phosphorus. Phosphine is absorbed by solutions of copper sulphate and mercuric chloride, forming phosphides of the metals.

(1) $$2PH_3+3CuSO_4=Cu_3P_2+3H_2SO_4$$

(2) $$2PH_3+3HgCl_2=Hg_3P_2+6HCl$$

It possesses like ammonia the property of combining with certain metallic chlorides such as aluminum chloride, stannic chloride, and antimony chloride.

15. Liquid Hydrogen Phosphide.—Liquid hydrogen phosphide, P_2H_4, was discovered by Thénard in 1845. It is obtained simultaneously with gaseous phosphine from which it is separated by cooling. It is a colorless, strongly refractive liquid and has a specific gravity of 1.012. It is spontaneously inflammable, burning with great brilliancy to phosphorus pentoxide, and boils at 57° C., leaving no residue if not heated too highly. On heating above its boiling point or on exposure to light, liquid phosphine decomposes into gaseous and solid phosphine.

16. Solid Hydrogen Phosphides.—There are two solid hydrogen phosphides, one compound having the formula P_4H_2 and the other the formula P_9H_2. The compound P_4H_2 is formed by the decomposition of liquid phosphine, as has just been stated, or by means of hydrochloric acid. It forms a yellow powder that burns when heated to 160° C., and has feeble acid properties. Heated to 70° C., in a stream of carbon dioxide it decomposes into hydrogen and phosphorus. When heated in a vacuum pure phosphine is evolved and there remains a residue of a red substance supposedly having the formula P_9H_2, thus:

$$5P_4H_2 = 2P_9H_2 + 2PH_3$$

Some doubt exists as to the existence of this compound, however, and it may be merely a complex mixture of red phosphorus and one of the other hydrides of phosphorus.

17. Phosphonium Compounds.—Phosphine acts like ammonia and combines with hydrobromic and hydriodic acids, forming salts. In these salts the group PH_4 acts like a metal and is termed phosphonium, just as the group NH_4 is called ammonium. The phosphonium compounds are not as stable as the ammonium compounds.

Phosphonium bromide, PH_4Br, is formed when hydrobromic acid and phosphine are brought together. The vapor has a

specific gravity of 1.906. The bromide crystallizes in colorless cubes, and boils at 30° C.

Phosphonium iodide, PH_4I, is best prepared by adding yellow phosphorus to a saturated solution of hydriodic acid and adding iodine after allowing this to stand for some hours. It can also be prepared by decomposing phosphorus di-iodide with a small quantity of water. The iodide forms large, transparent, glittering, quadratic prisms, fumes in the air, boils at 80° C., but vaporizes easily at lower temperatures. It is easily decomposed with water. Phosphonium iodide is used as a powerful reducing agent and as the basis for the preparation of many organic phosphorus compounds.

OXIDES AND ACIDS OF PHOSPHORUS

18. The common oxides and acids of phosphorus and the sodium salts of the acids are named as follows:

Oxides		Acids	
Phosphorus trioxide,	P_2O_3	Hypophosphorous acid,	H_3PO_2
Phosphorus tetroxide,	P_2O_4	Phosphorous acid,	H_3PO_3
Phosphorus pentoxide,	P_2O_5	Metaphosphoric acid,	HPO_3
		Hypophosphoric acid,	H_2PO_3
		Orthophosphoric acid,	H_3PO_4
		Pyrophosphoric acid,	$H_4P_2O_7$

Sodium Salts	
Sodium hypophosphite,	NaH_2PO_2
Sodium phosphite,	Na_2HPO_3
Sodium metaphosphate,	$NaPO_3$
Sodium hypophosphate,	Na_2PO_3
Sodium phosphate,	Na_3PO_4
Sodium pyrophosphate,	$Na_4P_2O_7$

19. Phosphorus Pentoxide.—Phosphorus pentoxide, P_2O_5, is always the product of the rapid combustion of phosphorus in the air or in oxygen The reaction may be expressed by the equation:

$$P_4+5O_2=2P_2O_5$$

It may be prepared as follows: Place under a large bell jar a flat china dish containing sulphuric acid, and leave this standing for about an hour or two, so as to dry thoroughly the air under the bell jar. Then remove the dish carefully without disturbing the air within the jar. A fragment of phosphorus about the size of a small pea, carefully dried between two pieces of blotting paper, is placed in a china saucer standing on a good-sized plate of glass and introduced under the bell jar, the phosphorus having been kindled with a hot wire. White fumes will fill the jar, and fall into the saucer and on the glass plate. The phenomenon resembles a miniature snow storm in appearance.

20. Properties.—Phosphorus pentoxide is a snowlike, amorphous substance. It is fusible at red heat and is readily volatilized. When plunged into water it hisses like a red-hot iron, but does not at once entirely dissolve, as a few flakes of metaphosphoric acid, HPO_3, always remain suspended in the liquid for some time. Its great feature is its attraction for water; left exposed to the air for a few minutes only, it deliquesces entirely, becoming converted into phosphoric acid. It is often used in laboratories as a dehydrating agent, and will even remove water from oil of vitriol. It has no action on dry blue litmus paper.

21. Orthophosphoric Acid.—Orthophosphoric acid, H_3PO_4, frequently designated merely as phosphoric acid, may be obtained in the laboratory by the action of boiling water on phosphorus pentoxide.

$$\underset{\substack{\text{phosphorus}\\\text{pentoxide}}}{P_2O_5} + \underset{\text{water}}{3H_2O} = \underset{\substack{\text{phosphoric}\\\text{acid}}}{2H_3PO_4}$$

Another method which may be employed for the preparation of phosphoric acid consists of oxidizing phosphorus with nitric acid, when the following reaction occurs:

$$\underset{\text{phosphorus}}{P_4} + \underset{\text{nitric acid}}{10HNO_3} + \underset{\text{water}}{H_2O} = \underset{\substack{\text{phosphoric}\\\text{acid}}}{4H_3PO_4} + \underset{\substack{\text{nitrogen}\\\text{trioxide}}}{5N_2O_3}$$

Pour into a beaker about 6 inches high 30 cubic centimeters of concentrated nitric acid and 15 cubic centimeters of water;

drop a few small pieces of phosphorus into the diluted acid and heat the whole gently. Nitrous fumes are given off and the phosphorus is dissolved. Should the action cease before the whole of the phosphorus has disappeared, add a little more acid. At the close of the reaction evaporate the liquid until it attains a temperature of 150° C. Phosphoric acid remains.

Commercially, an acid which is somewhat impure is prepared by treating bone ash (calcium phosphate) with sulphuric acid, as described under the manufacture of phosphorus. The reaction which takes place in this case, however, is represented as follows:

$$Ca_3(PO_4)_2+3H_2SO_4=3CaSO_4+2H_3PO_4$$

22. Properties.—Phosphoric acid, prepared as just explained, is a syrupy liquid which, upon being evaporated under diminished pressure or upon being heated to about 150°, loses the added water present and forms white, prismatic crystals, melting at 42.3° C., which deliquesce in the air. The concentrated aqueous solution of phosphoric acid is colorless and odorless. It is intensely acid in reaction, but is not nearly as active chemically as is a concentrated solution of sulphuric acid.

Phosphoric acid contains 3 replaceable hydrogen atoms. It is therefore tribasic and forms three kinds of salts, which may be represented and named as follows:

Empirical Formula	Supposed Structure
H_3PO_4	$\left.\begin{array}{l}HO\\HO\\HO\end{array}\right\rangle P=O$

The structural or graphic formula for phosphoric acid is written in this manner to show that each H atom is of equal value and that, no matter which one is replaced by a metal, the resulting compound will be the same, thus

$$\left.\begin{array}{l}NaO\\H\ O\\H\ O\end{array}\right\rangle P=O,\quad \left.\begin{array}{l}H\ O\\NaO\\H\ O\end{array}\right\rangle P=O,\ \text{and}\ \left.\begin{array}{l}H\ O\\H\ O\\NaO\end{array}\right\rangle P=O$$

are one and the same compound having the empirical formula NaH_2PO_4.

I L T 15D—26

23. As will subsequently be shown, some of the acids of phosphorus contain hydrogen atoms which are not replaceable by metals and in these instances the graphic formula represents a convenient method of illustrating the facts which have been demonstrated by actual experimental work to be true.

The three sodium salts of phosphoric acid are designated as follows:

Empirical Formula	Structural Formula	Name
NaH_2PO_4	NaO $H\ O \rightarrow P=O$ $H\ O$	monosodium phosphate or primary sodium phosphate or sodium dihydrogen phosphate
Na_2HPO_4	NaO $NaO \rightarrow P=O$ $H\ O$	disodium phosphate or secondary sodium phosphate or disodium hydrogen phosphate
Na_3PO_4	NaO $NaO \rightarrow P=O$ NaO	trisodium phosphate or tertiary phosphate or normal sodium phosphate

As in the case of sulphuric acid, the H atoms of orthophosphoric acid may be replaced by different metals or radicals; thus, the formation of sodium ammonium phosphate, $NaNH_4HPO_4{\cdot}4H_2O$, better known as microcosmic salt, is possible. Of these sodium salts, the primary is acid in its action toward litmus; the secondary is neutral; and the normal salt is alkaline.

PREPARATION OF SODIUM ORTHOPHOSPHATES

24. Disodium Phosphate.—Disodium phosphate, $Na_2HPO_4{\cdot}12H_2O$, may be prepared by adding a solution of sodium carbonate to dilute phosphoric acid until the resulting solution is slightly alkaline. The crystalline hydrate is then obtained by evaporating the solution and allowing it to cool. The reaction which takes place may be represented as follows:

$$Na_2CO_3+H_3PO_4+11H_2O=Na_2HPO_4{\cdot}12H_2O+CO_2$$

Disodium phosphate is ordinarily called sodium phosphate and is the reagent used in the determination of magnesium.

Upon heating the crystals to 100° C., they lose 12 molecules of water of crystallization.

25. Monosodium Phosphate.—Monosodium phosphate, $NaH_2PO_4 \cdot H_2O$, may be made by adding dilute phosphoric acid to a solution of disodium phosphate:

$$H_3PO_4 + Na_2HPO_4 + H_2O = 2NaH_2PO_4 \cdot H_2O$$

The crystalline salt is then obtained by evaporating and cooling the solution.

26. Trisodium Phosphate.—Trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$, is obtained by the action of sodium hydroxide on disodium phosphate:

$$NaOH + Na_2HPO_4 + 11H_2O = Na_3PO_4 \cdot 12H_2O$$

On evaporation of the resulting solution, the crystals are obtained. The water solution of this salt is alkaline in reaction, probably due to its splitting up into sodium hydroxide and disodium phosphate:

$$Na_3PO_4 + H_2O = Na_2HPO_4 + NaOH$$

MIXED PHOSPHATES

27. Sodium Ammonium Phosphate.—Sodium ammonium phosphate, or microcosmic salt, $NaNH_4HPO_4 \cdot 4H_2O$, may be obtained by mixing saturated solutions of ammonium chloride and disodium phosphate:

$$NH_4Cl + Na_2HPO_4 + 4H_2O = NaNH_4HPO_4 \cdot 4H_2O + NaCl$$

28. Magnesium Ammonium Phosphate.—Magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, is formed when soluble phosphates and sulphates or chlorides of magnesium are brought together in ammoniacal solution:

$$MgSO_4 + Na_2HPO_4 + NH_4OH + 5H_2O = Na_2SO_4 + MgNH_4PO_4 \cdot 6H_2O$$

29. Pyrophosphoric, or Diphosphoric, Acid.—When orthophosphoric acid is heated to 250° C., pyrophosphoric acid, $H_4P_2O_7$, is formed:

$$2H_3PO_4 - H_2O = H_4P_2O_7$$

Two molecules of orthophosphoric acid lose 1 molecule of water.

30. Pyrophosphoric acid generally occurs as a liquid, but may be obtained by evaporation at 213° C. as a soft glassy mass or in semicrystalline masses. Its solution is strongly acid, does not coagulate albumin, and gives a white precipitate with silver nitrate. Being tetrabasic, pyrophosphoric acid forms a large series of acid, normal, and double salts.

On boiling its solution, pyrophosphoric acid takes up a molecule of water and becomes orthophosphoric acid; on igniting, it loses 1 molecule of water, becoming metaphosphoric acid. The salts of pyrophosphoric acid are known as the pyrophosphates. They may be made by strongly igniting phosphates such as disodium phosphate or magnesium ammonium phosphate:

$$2Na_2HPO_4 + \text{heat} = Na_4P_2O_7 + H_2O$$
$$2MgNH_4PO_4 + \text{heat} = Mg_2P_2O_7 + H_2O + 2NH_3$$

31. Metaphosphoric Acid.—In 1833, Graham showed that phosphoric acid loses water on being strongly heated and that on cooling it becomes a transparent icelike solid which he named glacial phosphoric acid, but which is today known as metaphosphoric acid, HPO_3.

$$H_3PO_4 - H_2O = HPO_3$$

This acid is also prepared by dissolving phosphorus pentoxide in cold water:

$$P_2O_5 + H_2O = 2HPO_3$$

Metaphosphates are produced by igniting primary phosphates:

$$NaH_2PO_4 - H_2O = NaPO_3$$

or phosphates that have 2 molecules of volatile base:

$$\underset{\substack{\text{sodium ammonium}\\ \text{phosphate}}}{2NaNH_4HPO_4} = \underset{\substack{\text{ammonium}\\ \text{hydroxide}}}{2NH_4OH} + \underset{\substack{\text{sodium}\\ \text{metaphosphate}}}{2NaPO_3}$$

32. Metaphosphoric acid, HPO_3, is obtained by decomposing metaphosphates. It is a transparent, colorless, hard, glasslike compound that though very soluble in water is not

crystallizable. Dissolved in water, it forms a strongly acid solution that gradually takes water from the air and forms orthophosphoric acid; this transformation is hastened by boiling. It possesses the property of coagulating albumin—a property that phosphoric acid does not possess—and gives a white precipitate with silver nitrate. Being monobasic, it forms but one class of salts. When the aqueous solutions of these salts are boiled, they are converted into primary orthophosphates. It is distinguished by a remarkable tendency to produce polymeric forms called di-, tri-, tetra-, and hexa-metaphosphates.

33. Phosphorus Trioxide.—Phosphorus trioxide, or phosphorous anhydride, P_2O_3, is formed by burning phosphorus in a limited supply of air, as by putting a piece of phosphorus in the glass tube, as shown in Fig. 3, drawing air through the tube, and at the same time warming it gently. In this way sufficient air is not brought in contact with the phosphorus to form the pentoxide. Phosphorus trioxide is thus obtained as

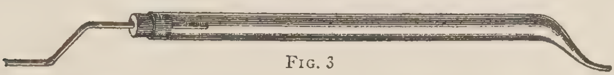


FIG. 3

a waxlike mass. It may also be condensed in the form of feathery crystals. Phosphorus trioxide has an unpleasant garlic-like odor, melts at 22.5° C., and boils at 173° C. When pure it is unaltered by light, but when impure it changes to a dark-red color, due to the separation of red phosphorus. On exposure to the air, it is slowly oxidized to the pentoxide and when brought in contact with oxygen or chlorine, it takes fire. In contact with cold water, phosphorous acid, H_3PO_3, is formed while hot water decomposes the oxide, red phosphorus and phosphine being among the decomposition products.

34. Phosphorous Acid.—Phosphorous acid, H_3PO_3, as already stated, is formed by the action of cold water on phosphorus trioxide, thus:

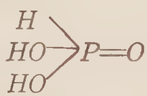
$$P_2O_3+3H_2O=2H_3PO_3$$

It may also be prepared by the action of water on phosphorus trichloride, PCl_3:

$$PCl_3+3H_2O=H_3PO_3+3HCl$$

At ordinary temperatures, phosphorous acid is a crystalline solid which melts at 70.1° C. The crystals of the acid may be obtained by evaporating the solution obtained as the result of the above reactions until a temperature of about 185° C. is reached. Upon cooling this concentrated solution, the acid crystallizes.

Phosphorous acid is a powerful reducing agent. When added to aqueous solutions of copper sulphate, silver nitrate, or gold chloride, the metals copper, silver, and gold are precipitated in the metallic state. Although the empirical formula of phosphorous acid is accepted as H_3PO_3, up to the present time all of the evidence points to the fact that the acid is dibasic and that, therefore, one of the hydrogen atoms cannot be replaced. Here again the graphic formula illustrates the point and, as in the case of phosphoric acid, the hydrogen atoms united to oxygen are replaceable, and the formula may be written as follows:



The salts of phosphorous acid are known as phosphites.

35. Hypophosphorous Acid.—Hypophosphorous acid, H_3PO_2, may be prepared by the action of sulphuric acid on barium hypophosphite, $BaH_4P_2O_4$. The latter compound is prepared by boiling phosphorus in a solution of barium hydroxide:

$$2P_4+3Ba(OH)_2+6H_2O=2PH_3+3BaH_4P_2O_4$$

and upon treating the barium hypophosphite with sulphuric acid, hypophosphorous acid is set free and barium sulphate precipitated:

$$BaH_4P_2O_4+H_2SO_4=2H_3PO_2+BaSO_4$$

The barium sulphate is then removed either by filtering or by decanting the solution and the latter or the filtrate is then evaporated, cooled, and the hypophosphorous acid allowed to crystallize. Crystals of pure hypophosphorous acid melt at 26.5° C. Hypophosphorous acid, like phosphorous acid, is a

powerful reducing agent, the salts of gold, silver, and mercury being reduced to the metallic state while with copper sulphate a precipitate of copper hydride, Cu_2H_2, is formed.

In spite of the 3 hydrogen atoms shown by the empirical formula, this acid is monobasic and the graphic formula may be written:

$$\left.\begin{matrix}H\\H\\HO\end{matrix}\right\rangle P{=}O$$

Since only one of the hydrogen atoms of hypophosphorous acid is replaceable by metals, the residue, or H_2PO_2, may be said to act as a radical, as does SO_4 or PO_4. Thus, the formula for barium hypophosphite may be written $Ba(H_2PO_2)_2$, and that of sodium hypophosphite, NaH_2PO_2.

36. Phosphorus Tetroxide.—Phosphorus tetroxide, P_2O_4, is formed along with red phosphorus when phosphorus trioxide is heated to 440° C. If the heating is done in a sealed tube, the tetroxide appears in the form of colorless crystals in the cooler parts of the tube. These crystals react with water to form phosphoric and phosphorous acids:

$$P_2O_4+3H_2O=H_3PO_4+H_3PO_3$$

37. Hypophosphoric Acid.—Hypophosphoric acid, H_2PO_3, or $H_4P_2O_6$, may be formed by the slow oxidation of phosphorus as by the action of moist air and the oxidation of phosphorus in a solution of copper nitrate containing free nitric acid. The solution so obtained is then half neutralized with sodium hydroxide, the acid salt, sodium acid hypophosphate, $Na_2H_2P_2O_6{\cdot}6H_2O$, crystallizing upon standing. The acid is obtained indirectly from this salt by treating an aqueous solution of it with barium chloride. A precipitate of barium hypophosphate is thus obtained:

$$Na_2H_2P_2O_6+BaCl_2=BaH_2P_2O_6+2NaCl$$

which, when treated with sulphuric acid, gives a solution of the free acid:

$$BaH_2P_2O_6+H_2SO_4=H_4P_2O_6+BaSO_4$$

The barium sulphate is removed by filtration and the acid solution evaporated at 30° C. under diminished pressure. The syrup-like product is then placed in a vacuum desiccator over concentrated sulphuric acid and upon standing yields crystals of the anhydrous acid. These crystals melt at 55° C. and decompose at 70° C.

HALOGEN COMPOUNDS OF PHOSPHORUS

38. Phosphorus unites with the halogens to form compounds of the types PX_3 and PX_5, in which X represents the halogen atom. The most important of the halogen compounds of phosphorus are the chlorides.

39. Phosphorus Trichloride.—Phosphorus trichloride, PCl_3, is made by passing dry chlorine over melted white phosphorus in a suitable apparatus until a gain in weight proportionate to that required by the equation:

$$P_4+6Cl_2=4PCl_3$$

is obtained.

Phosphorus trichloride is a volatile liquid, boiling at 74° C. and possessing a pungent odor. It has a specific gravity of 1.61.

40. Phosphorus Pentachloride.—Phosphorus pentachloride, PCl_5, is made in almost the same manner as the trichloride. If chlorine in excess is passed over phosphorus, or if the chlorine be allowed to act on phosphorus trichloride, the resulting product is phosphorus pentachloride.

Phosphorus pentachloride is a solid substance usually obtained in the form of a powder which does not melt at any temperature under atmospheric pressure, but passes directly from the solid to the vapor state when heated from 160° C. to 165° C. In other words, this compound sublimes. Under slight pressure it may be melted at 148° C.

41. When brought in contact with water, phosphorus pentachloride decomposes, phosphoric acid and hydrochloric acid being formed:

$$PCl_5+4H_2O=H_3PO_4+5HCl$$

When only traces of water are present, however, the decomposition products are hydrochloric acid and phosphorus oxychloride, $POCl_3$.

$$PCl_5+H_2O=POCl_3+2HCl$$

This reaction of phosphorus pentachloride takes place with most compounds containing the hydroxyl (OH) group, and is used as a test, especially in organic chemistry, as a means of determining whether or not the hydroxyl group is present in the structure of an unknown carbon compound.

Of the halides of phosphorus, other than the chlorides known to exist, are the tribromide, PBr_3, a liquid; the tri-iodide, PI_3, a solid; and the trifluoride, PF_3, a gas. Of the pentahalogen compounds, the bromide, PBr_5, is a solid and the fluoride, PF_5, is a gas. The compound PI_5 is unknown, but the existence of phosphorus di-iodide, P_2I_4, a solid compound, has been established.

As in the case of the trichloride and pentachloride, all of the halogen compounds of phosphorus may be made by a direct union of the elements.

42. Phosphorus Oxychloride.—Phosphorus oxychloride, $POCl_3$, is also called phosphoryl chloride and, as previously stated, it may be made by treating phosphorus pentachloride with small quantities of water. Small quantities may also be prepared by passing phosgene gas, $COCl_2$, over calcium phosphate, $Ca_3(PO_4)_2$, contained in a tubular furnace heated to about 500° C. The reactions which take place are probably as follows:

(1) $$Ca_3(PO_4)_2+2COCl_2=Ca(PO_3)_2+2CO_2+2CaCl_2$$

(2) $$Ca(PO_3)_2+4COCl_2=2POCl_3+4CO_2+CaCl_2$$

Phosphorus oxychloride has a specific gravity of 1.71 and boils at 107.2° C. The oxychlorides of bromine and fluorine are also known.

SULPHIDES OF PHOSPHORUS

43. At least two sulphides of phosphorus are known. They are the pentasulphide, P_2S_5, and tetraphosphorus trisulphide, P_4S_3. Both are made by the direct union of phosphorus and

sulphur brought about by heating a mixture of the two elements. When yellow phosphorus is used the reaction takes place violently; therefore, the red variety is employed.

Phosphorus pentasulphide is a yellow crystalline solid which melts at 290° C. and boils at 520° C. The trisulphide melts at 172° C. and boils at 408° C.

ARSENIC

Symbol As. Atomic weight 74.96. Molecular formula As_4. Molecular weight 299.84.

44. History and Occurrence.—While arsenic is a perfect analog of phosphorus, it at the same time possesses a metallic luster and conducts electricity. In its free state it is very similar to the metals. Sulphides and the oxides of arsenic have been known for many years. Brandt in 1773 was the first to examine arsenic carefully and to give it a place among the non-metals.

Arsenic occurs widely distributed both native and in combination with metals. Most sulphides of zinc and iron contain arsenic, hence it is very frequently found in these metals and in sulphuric acid made from the sulphide ores of these metals. Arsenic occurs most frequently as the sulphides, realgar, As_2S_2, and orpiment, As_2S_3; also as mispickel, $FeAsS$; arsenical iron and nickel, $FeAs_2$, $NiAs_2$; smaltite, $CoAs_2$; and proustite, $3Ag_2S{\cdot}As_2S_3$. Arsenic is obtained in considerable quantities in the form of arsenious oxide as a by-product in the working of gold, silver, and lead ores.

45. Preparation and Properties.—Arsenic is obtained from its natural sulphides, by heating them in earthen retorts; the arsenic, being volatile, sublimes and condenses in the cooler portions of the retort, toward its mouth. Thus,

$$4FeAsS + \text{heat} = As_4 + 4FeS$$

In certain districts, arsenic is obtained by reducing its oxide with charcoal—a method by which it is obtained in a much purer form. Thus,

$$2As_2O_3 + 6C = As_4 + 6CO$$

Ordinary arsenic presents the appearance of a dark, steel-gray brittle solid possessing a distinctly metallic luster and having a specific gravity of 5.727. It occurs in three allotropic modifications. Besides the steel-gray variety, which crystallizes in rhombohedrons and possesses the above-mentioned specific gravity, there is an amorphous, black, vitreous variety, of specific gravity 4.71, which at 360° C. passes into the crystalline variety with the evolution of much heat.

46. The third modification is called yellow arsenic. It is formed when arsenic vapor is quickly condensed. This variety has a specific gravity of 3.70 and is quickly converted into the ordinary or gray variety upon exposure to light. Arsenic may be sublimed when heated to 554° C., and melted under pressure at 850° C. If ignited at 180° C., it burns with a bluish-white flame, arsenic trioxide, As_2O_3, being formed. Arsenic vapors are yellow in color and possess an odor resembling that of garlic. Arsenic and all its compounds are active poisons.

ARSENIC AND HYDROGEN

47. Arsine, or Hydrogen Arsenide.—The compound arsine, AsH_3, is formed by the action of nascent, or atomic, hydrogen on solutions of arsenic compounds. Nascent hydrogen (written H) may be formed by the action of HCl or H_2SO_4 on zinc; thus,

$$Zn+2HCl=ZnCl_2+2H$$

When this hydrogen acts on solutions of arsenic compounds arsine is formed; thus,

$$As_2O_3+12H=3H_2O+2AsH_3$$

Arsine is also formed by the action of hydrochloric or sulphuric acid on zinc arsenide, thus:

$$Zn_3As_2+6HCl=2AsH_3+3ZnCl_2$$

Arsine is an extremely poisonous, colorless gas with a strong garlic-like odor, having a specific gravity of 2.7. It may be condensed to a liquid at $-54.8°$ C. and frozen to a solid which melts at $-113.5°$ C. It takes fire readily in the air, burning with a bluish-white flame and evolving white fumes of arsenic

trioxide. If a cold surface of porcelain is held in this flame, metallic arsenic is deposited on it as a dark stain, or tache. Arsine is readily decomposed when the tube through which it is passing is heated to redness, a dark mirror-like ring of metallic arsenic being formed just beyond the heated spot. The gas is also decomposed when passed into a dilute solution of silver nitrate, forming arsenious acid and precipitating metallic silver:

$$AsH_3+6AgNO_3+3H_2O=6Ag+6HNO_3+H_3AsO_3$$

48. Marsh Test for Arsenic.—The importance of arsine lies in its application for the detection of arsenic in what is known as Marsh's test, which depends on the production of arsine whenever arsenic is in a solution in which nascent hydrogen is formed.

A convenient form of Marsh's apparatus is shown in Fig. 4. It consists of a three-necked Woulff's bottle A through the

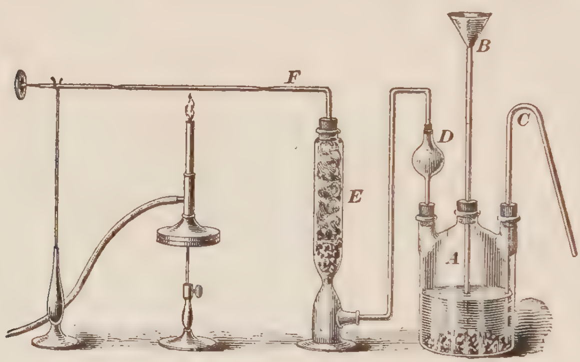


FIG. 4

middle tubulure of which a funnel B passes for the supply of liquid, while one of the side openings has a siphon tube C for withdrawing the exhausted acid, and the other tubulure has a delivery tube with a bulb D. This bulb is filled with cotton to retain any impurities that might be mechanically carried over by the gas. Attached to this delivery tube is a jar E filled with potassium hydroxide and calcium chloride; the object of this mixture is to purify the evolved gas which then passes through another delivery tube F.

Small pieces of pure zinc are first placed in the Woulff's bottle to which is added pure sulphuric acid previously diluted with 3 parts of distilled water and thoroughly cooled (so as to have normal temperature). After allowing sufficient time for the air to be expelled from the apparatus, the hydrogen escaping through the tube *F* is ignited. This tube is then heated to dull redness by a Bunsen burner flame. If no dark deposit appears beyond the flame in 15 minutes, the materials employed may be considered free from arsenic. The liquid supposed to contain arsenic is then added through the funnel tube. If arsenic should be present, a metallic mirror will be formed in the tube within 15 minutes. If the tube *F* is not heated, the flame of hydrogen burning at its end will often in a few seconds change its color, becoming whitish, and will form a steel-gray or black metallic spot on a glazed porcelain plate held in it.

OXIDES AND ACIDS OF ARSENIC

49. The oxides of arsenic, with their corresponding acids, are:

Oxides	Acids
Arsenic trioxide, As_2O_3	Arsenious acid, H_3AsO_3
Arsenic pentoxide, As_2O_5	Arsenic acid, H_3AsO_4

50. Arsenic Trioxide.—Arsenic trioxide, As_2O_3, or arsenious anhydride, has long been known under the names of white arsenic and arsenious acid. It is prepared by the roasting of ores containing arsenic, the vapors given off being condensed in long brick chambers, where they condense in the form of a white powder. It is purified by again subliming and recondensing. Arsenic trioxide occurs in three distinct modifications, designated as vitreous, octahedral, and rhombic or monoclinic. When arsenic-trioxide vapor is condensed at a temperature of 400° C., it forms a transparent vitreous mass of a specific gravity of 3.738. If this modification is allowed to stand exposed to the air, crystals of the octahedral variety are slowly formed. This variety is also obtained either by condensing the vapor at 200° C., or by cooling a saturated aqueous

solution of arsenic trioxide of the first modification, as brilliant transparent octahedral crystals of specific gravity 3.689.

Again when the vitreous modification is dissolved to saturation in hot hydrochloric acid and left to cool slowly, it crystallizes in octahedrons, the formation of each crystal being accompanied by a flash of light.

51. When the crystallization is carried out above 200° C., the rhombic or, as it is sometimes called, monoclinic variety is obtained. This kind is also formed upon heating either of the other two modifications at 200° C., for an extended period, or by crystallization from a hot saturated solution of the trioxide in potassium hydroxide. This variety of arsenic trioxide has a specific gravity of 4.15.

All varieties of arsenic trioxide are volatilized at 218° C.; they are sparingly soluble in water, but are more soluble in hydrochloric acid and in alkaline solutions.

Arsenic trioxide is frequently mistaken for flour, but it may be easily recognized by its weight and by sprinkling it on red-hot coal, when a strong odor of garlic is obtained.

52. Arsenic trioxide is only slightly soluble in water. The solution has a sweet, unpleasant metallic taste, is feebly acid, and is very poisonous. The best antidote for arsenic in any form is freshly precipitated ferric hydroxide. Workers in arsenic plants usually apply an ointment of ferric hydroxide and lanoline to their faces previous to beginning work. The ferric hydroxide is best precipitated by means of magnesium hydroxide from a solution of a ferric salt. Ferric hydroxide forms an insoluble arsenite with the arsenic and thus prevents further absorption of the poison. The reaction of ferric hydroxide and arsenic is represented by the following equation:

$$Fe(OH)_3 + H_3AsO_3 = FeAsO_3 + 3H_2O$$

53. Arsenious Acid.—Arsenious acid, H_3AsO_3, is obtained when arsenic trioxide is dissolved in water. It has never been prepared in a pure state, as the solution is probably a solution of the trioxide. This solution has a slight acid reaction and forms salts called arsenites.

By adding just enough ammonia to neutralize the solution and then adding silver-nitrate solution, a salt is obtained corresponding to the formula Ag_3AsO_3, which shows the acid to be tribasic.

Several series of arsenites are known, namely, ortho-arsenites, meta-arsenites, and pyro-arsenites.

The alkali arsenites are soluble in water, absorb oxygen from the air, showing they are powerful reducing agents; they themselves are converted into arsenates. The alkali arsenites are frequently used in sheep dips and in sprays, and a soap containing these salts together with other ingredients is sometimes used to preserve the skins of animals.

54. Scheele's Green, or Copper, Arsenite.—Scheele's green, $CuHAsO_3$, is formed when arsenious acid is dissolved in a solution of potassium carbonate and a solution of copper sulphate is added. Thus,

$$H_3AsO_3+K_2CO_3+CuSO_4=CuHAsO_3+K_2SO_4+CO_2+H_2O$$

It is a very poisonous pigment sometimes used in the manufacture of wallpaper.

55. Reinch's Test for Arsenic in Wallpaper.—The sample of paper is soaked for some time in ammonium hydroxide, which dissolves copper arsenite. The solution is then acidified with hydrochloric acid, which should compose at least one-tenth of the volume of the solution, and boiling this with a strip of bright copper, the arsenic is deposited on the copper as a gray film. To further identify the deposit, wash the copper with distilled water, dry, and heat in a glass tube, to obtain the arsenic mirror or the crystalline structure. All the reagents used must be tested for arsenic in the same manner to be perfectly sure that the arsenic is in the wallpaper.

56. Paris Green and Fowler's Solution.—Other well-known arsenites are Paris green, or Schweinfurt green, which is a copper aceto-arsenite made by mixing equal parts of hot solutions of arsenic trioxide and copper acetate. The formula of this compound is probably $Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$. Fowler's solution is prepared by dissolving

arsenic trioxide in a solution containing twice its weight of potassium bicarbonate. The reaction which takes place may be represented as follows:

$$As_2O_3+4KHCO_3=2K_2HAsO_3+4CO_2+H_2O$$

57. Arsenic Pentoxide.—Although arsenic resembles phosphorus very closely, it differs from the latter in this respect that when burned in air or oxygen it oxidizes to the trioxide only. Arsenic pentoxide may be prepared directly from arsenic acid, H_3AsO_4, by heating the latter to 210° C., for several hours. In this way it is obtained in the form of a white, glassy solid which deliquesces in air.

Arsenic pentoxide has a specific gravity varying from 3.99 to 4.25. It dissolves slowly in water, forming arsenic acid. Heated to above 450° C., it decomposes into oxygen and arsenic trioxide, and heated with reducing agents, it is easily reduced to free arsenic.

58. Arsenic Acid.—Arsenic acid, $H_3AsO_4.H_2O$, was first prepared by Scheele in 1775 by the oxidation of arsenic trioxide with nitric acid. He also prepared it by the action of moist chlorine gas on the trioxide, thus:

$$As_2O_3+5H_2O+2Cl_2=2H_3AsO_4+4HCl$$

After evaporation long rhomboidal crystals having the formula $2H_3AsO_4 \cdot H_2O$, are obtained from the cold solution. These crystals deliquesce in the air and when heated to 100° C., they lose their water of crystallization and yield an acid having the formula $H_5As_3O_{10}$, and when this compound is strongly heated it breaks up into arsenic pentoxide and water. Thus, although the salts of orthoarsenic, pyroarsenic, and metarsenic acids are known, the acids themselves have never been obtained.

HALOGEN COMPOUNDS OF ARSENIC

59. The compounds of arsenic with the halogens are analogous with the corresponding phosphorus compounds. They are the result of the direct union of their constituents. The slight metallic character of arsenic is shown in the chloride

which may be formed by the action of hydrochloric acid on the oxide.

60. Arsenic Trichloride.—Arsenic trichloride, $AsCl_3$, is prepared by distilling arsenic trioxide with strong hydrochloric acid:

$$As_2O_3+6HCl=2AsCl_3+3H_2O$$

It can also be prepared by passing dry chlorine over white arsenic heated in a retort. The trichloride is then distilled over into a flask leaving a transparent glassy mass behind.

Arsenic trichloride is a colorless, oily liquid with a specific gravity of 2.16 at 20° C. It boils at 130° C., evolving a heavy, colorless vapor, and solidifies in long, pearly needles at −18° C. Exposed to the air, it gives off dense white fumes, which are extremely poisonous. A small quantity of water dissolves arsenic trichloride without change but considerable water decomposes it into hydrochloric acid and arsenic trioxide, thus:

$$2AsCl_3+3H_2O=As_2O_3+6HCl$$

The existence of arsenic pentachloride, $AsCl_5$, has not been definitely established.

61. Arsenic Tribromide and Tri-iodide.—Arsenic tribromide, $AsBr_3$, and arsenic tri-iodide, AsI_3, are prepared in the same manner as the trichloride. The tribromide forms colorless, deliquescent crystals that melt at 31° C. and boil at 220° C. It has a strong odor of arsenic and is acted on by water in the same way as the trichloride. Arsenic tri-iodide forms bright-red, hexagonal crystals, of a specific gravity of 4.4, and that melt at 140.7° C.

62. Arsenic forms two fluorides, the trifluoride, AsF_3, and the pentafluoride, AsF_5. The former is prepared by distilling arsenic trioxide with fluorspar and sulphuric acid. It is a transparent, colorless liquid that fumes strongly in the air; it has a powerful, pungent odor, solidifies at −8.5° C., boils at 63° C., and is decomposed by water. The pentafluoride is formed by distilling a mixture of arsenic trifluoride, antimony pentafluoride, and bromine. It is a colorless gas that liquefies at −53° C. and becomes solid at −80° C.

SULPHIDES OF ARSENIC

63. Three sulphides of arsenic are known. They are arsenic disulphide, or realgar, As_2S_2; arsenic trisulphide, or orpiment, As_2S_3; and arsenic pentasulphide, As_2S_5.

64. Realgar.—Realgar, or arsenic disulphide, As_2S_2, occurs in nature in the form of transparent red crystals of the type of the oblique rhombic prism. It is formed artificially by heating arsenic acid with the proper proportion of sulphur. It is fusible and may be crystallized by slow cooling. When strongly heated in a closed vessel, it boils and distils without alteration, but when heated in the air it burns into arsenic trioxide and sulphur dioxide. The alkaline sulphides and ammonium sulphide dissolve realgar, leaving a brown powder that is considered a subsulphide of arsenic. A boiling solution of potassium hydroxide also dissolves realgar, forming a mixture of potassium arsenite and sulpharsenite; the latter is a soluble compound of arsenic trisulphide and potassium sulphide.

65. Arsenic Trisulphide.—Arsenic trisulphide, or orpiment, As_2S_3, is found in nature in yellow prismatic crystals. It may be obtained by fusing arsenic and sulphur together in the proper proportion, or arsenic trioxide and sulphur; in the latter case, sulphur dioxide is disengaged and arsenic trisulphide sublimes. Thus prepared, orpiment occurs as a crystalline orange-yellow compound. It is fusible and volatile, burning with a pale-blue flame.

66. Arsenic Pentasulphide.—Arsenic pentasulphide, As_2S_5, is precipitated when an excess of hydrogen sulphide is passed into a solution of arsenic acid heated to 70° C. It is a lemon-yellow powder that is insoluble in water and may be fused and distilled without alteration.

ANTIMONY

Symbol Sb. Atomic weight 120.2. Molecular formula Sb_2. Molecular weight 240.4.

67. History and Occurrence.—Antimony has been known for many hundred years; it was prepared in the pure state by Basil Valentine toward the end of the 15th century. It occurs in nature both free and in combination. Its most abundant source is the sulphide known as stibnite, found in China, Japan, Australia, the East Indies, and Hungary. It also exists in combination with oxygen in the minerals valentinite, senarmontite, and cervantite, with silver in dyscrasite; and with silver and sulphur in pyrargyrite and miargyrite.

68. Preparation and Properties.—Antimony is obtained from its sulphide, Sb_2S_3, by heating it in covered pots with metallic iron:

$$Sb_2S_3+3Fe=3FeS+Sb_2$$

The excess of iron is removed by heating with charcoal and fluxes such as sodium carbonate, and a further addition of the sulphide. The metal extracted in this way is contaminated with arsenic, iron, sulphur, and often lead or copper. It may be further purified by remelting with potassium hydroxide when, on solidifying, it shows fernlike markings due to crystallization, and is known as star metal.

It is prepared also by roasting the sulphide, when the sulphur burns and antimony trioxide is formed. The oxide is then reduced with carbon. Thus,

$$2Sb_2S_3+9O_2=2Sb_2O_3+6SO_2$$
$$2Sb_2O_3+3C=2Sb_2+3CO_2$$

69. Antimony is a brilliant, bluish-white, brittle element, of specific gravity 6.715. It crystallizes in rhombohedrons, thus being isomorphous with arsenic and red phosphorus. It melts at 630° C. and at a white heat may be distilled. It scarcely tarnishes in the air, but takes fire at a red heat, producing antimony trioxide. It is strongly attacked by chlorine, forming antimony trichloride, $SbCl_3$, and pentachloride, $SbCl_5$. Anti-

mony is so brittle that its only use in the free state is for the construction of thermoelectric piles. It is used in several useful alloys, however, as, for example, in type metal, Britannia metal, pewter, in pharmacy, and in calico dyeing and printing.

ANTIMONY AND HYDROGEN

70. Stibine.—Antimony and hydrogen form a compound known as stibine, SbH_3, which is similar to the hydrogen compounds of nitrogen, phosphorus, and arsenic in constitution, but it resembles arsine very closely. Stibine is a colorless, peculiarly disagreeable smelling, poisonous gas. It can be condensed to a colorless liquid that boils at $-18°$ C. and solidifies at about $-91°$ C. It is slightly soluble in water and is very easily ignited, burning with a greenish-white flame and giving off white fumes of the trioxide.

Whenever an antimony compound is present in a solution from which hydrogen is being evolved (see Marsh test for arsenic) a gas escapes, mixed with the hydrogen, causing it to burn with a bluish-white flame. This gas is stibine, which is like arsine decomposed by heat, but the metallic deposit of antimony is easily distinguished from that of arsenic by being less volatile, by its darker color, its smoky appearance, its insolubility in hypochlorites, and its solubility in ammonium sulphide.

OXIDES AND ACIDS OF ANTIMONY

71. The three oxides and three acids of antimony known are:

Oxides		Acids	
Antimony trioxide,	Sb_2O_3	Orthoantimonic acid,	H_3SbO_4
Antimony tetroxide,	Sb_2O_4	Metantimonic acid,	$HSbO_3$
Antimony pentoxide,	Sb_2O_5	Pyroantimonic acid,	$H_4Sb_2O_7$

72. Antimony Trioxide.—Antimony trioxide, Sb_2O_3, occurs in nature as valentinite, or white ore of antimony. It is the product of the combustion of antimony in air or of its oxidation by nitric acid. The trioxide formed by burning

antimony in air always contains some tetroxide, and by heating it long enough at a sufficiently high temperature it is completely converted into the tetroxide. Toward some of the stronger bases like sodium hydróxide the trioxide acts as an acidic oxide. Toward most bases, however, it does not show acid properties, and toward the stronger acids it acts as a base. Oxidizing agents convert it into antimonic acid.

73. Antimony Tetroxide.—Antimony tetroxide, Sb_2O_4, as previously stated, may be prepared by igniting the trioxide in the air. It occurs native as antimony ochre. It can be obtained more readily by igniting antimonic acid, H_3SbO_4, thus driving off water and oxygen. At ordinary temperatures the tetroxide is white, but becomes yellow when heated. It has the properties of an acidic oxide toward strong bases, but toward strong acids it acts as a weak base.

74. Antimony Pentoxide.—Antimony pentoxide, Sb_2O_5, is prepared by gently igniting antimonic acid to expel water, but care must be taken not to heat it high enough to expel oxygen. It cannot be formed by the addition of oxygen to the tetroxide, but if ignited, easily breaks up into the tetroxide and oxygen.

75. Acids of Antimony.—Antimonic acid, H_3SbO_4, is the final oxidation product when antimony is treated with aqua regia. It may also be obtained by treating one of its salts with sulphuric acid. It is similar to phosphoric and arsenic acids and occurs in three forms. The ortho acid, H_3SbO_4, is formed when antimony pentachloride is decomposed with water. When dried at 100° C., the pyro acid, $H_4Sb_2O_7$, is formed, and when heated to 200° C. the meta acid, $HSbO_3$, results. The ortho and meta acids are white amorphous bodies soluble in potassium hydroxide and only slightly soluble in water. The pyro acid, while only sparingly soluble in water, is more soluble than is the meta; the normal alkali salts of the pyro acid are soluble in water.

ANTIMONY AND CHLORINE

76. Antimony Trichloride.—Antimony trichloride, $SbCl_3$, may be prepared by treating antimony directly with chlorine or by dissolving antimony in hydrochloric acid with the addition of nitric acid and distilling the product. This compound is a solid crystalline substance that is quite soft, and on account of its consistency is called butter of antimony. It melts at 73° C., boils at 223° C., and deliquesces in the air. When treated with water an oxychloride is formed the composition of which depends more or less on the temperature of the water. Thus,

$$SbCl_3+H_2O \text{ (cold)} = 2HCl+SbOCl \text{ (antimonyl chloride)}$$
$$4SbCl_3+5H_2O \text{ (hot)} = (SbOCl)_2Sb_2O_3+10HCl$$

If free hydrochloric or tartaric acid is present, precipitation is prevented.

77. Antimony Pentachloride—Antimony pentachloride, $SbCl_5$, may be obtained by treating the trichloride with an excess of chlorine. It is similar to phosphorus pentachloride, but is more readily converted into the trichloride according to the equation:

$$SbCl_5=SbCl_3+Cl_2$$

This is similar to the action of the pentoxide of phosphorus in breaking down into the trioxide and oxygen. When the pentachloride is acted on by water it at first yields an oxychloride, but by further action it yields antimonic acid, H_3SbO_4. Thus:

$$SbCl_5+H_2O=SbOCl_3+2HCl$$
$$SbOCl_3+3H_2O=H_3SbO_4+3HCl$$

ANTIMONY AND SULPHUR

78. Antimony Trisulphide.—Antimony trisulphide, Sb_2S_3, occurs in nature as the mineral stibnite, and is the chief ore of antimony. It may be prepared by treating a solution of antimony trichloride with hydrogen sulphide, when the trisulphide separates as an orange-colored precipitate. The naturally

occurring trisulphide is either gray or black. The reaction is as follows:

$$2SbCl_3+3H_2S=Sb_2S_3+6HCl$$

79. Antimony Pentasulphide.—Antimony pentasulphide, Sb_2S_5, may be prepared by passing hydrogen-sulphide gas into a solution of antimony chloride, acidified with HCl. Thus,

$$2SbCl_5+5H_2S=Sb_2S_5+10HCl$$

When dry this compound appears as a golden-yellow powder.

BISMUTH

Symbol Bi. Atomic weight 208. Molecular formula Bi_2. *Molecular weight 416.*

80. History and Occurrence.—Bismuth was first distinctly recognized by Basil Valentine in the 15th century. Agricola in 1529 called it bismetum, and Paracelsus mentions it as wismeat. It was for a long time confounded with other elements, especially with lead, tin, and antimony. Pott in 1739 first described its characteristic actions. This element occurs in the native condition in veins traversing gneiss, clay, slate, and other crystalline rocks. It also occurs as oxide, forming the mineral bismite; as sulphide, or bismuthinite; as sulphotelluride, or tetradymite; and as carbonate, or bismutite.

81. Preparation and Properties.—Bismuth for use in the arts is obtained on a large scale from the native bismuth by placing this, mixed with the rocky gangue, in iron tubes slightly inclined, which are heated in a furnace. The bismuth melts and flows out at the lower ends of the tubes into suitable vessels from which it is ladled into molds. The bismuth of commerce is mostly contaminated with arsenic, iron, and various other metals, from which it may be freed by fusion with potassium nitrate. Chemically pure bismuth may be obtained by reducing bismuth nitrate, $Bi(NO_3)_3$, with charcoal.

Bismuth is a hard, brittle, brilliant metal of a reddish-white color. It has a great tendency to crystallize on fusion. By

melting a considerable quantity of it, allowing it to cool until a crust forms on the surface, piercing this and pouring out the portion that still remains liquid, crystals of great size and beauty may be obtained. Owing to a slight superficial oxidation, these crystals as usually obtained are beautifully iridescent. Bismuth has a specific gravity of 9.747; it melts at 268° C. and expands one thirty-second of its bulk in solidifying. It may be distilled at a white heat. It is unaltered in dry air, but is tarnished in the presence of moisture. Strongly heated it takes fire, burning with a bluish-white flame and forming bismuth trioxide, Bi_2O_3. Chlorine and nitric acid attack it readily, but cold hydrochloric and sulphuric acids have no action upon it.

Bismuth is used in the arts chiefly for forming alloys. Rose's fusible metal is composed of 1 part of lead, 1 of tin, and 2 of bismuth; it melts at 94° C. Lipowitz's fusible metal contains 3 parts of cadmium, 4 of tin, 8 of lead, and 15 of bismuth; it melts at 60° C. Bismuth is also employed to some extent in medicinal preparations.

OXIDES AND ACIDS OF BISMUTH

82. There are four oxides of bismuth, and one acid that has the form of metarsenic and metantimonic acids, and is generally called *bismuthic acid*. These compounds have basic rather than acidic properties, showing that bismuth should be considered a base-forming element. Though its metallic characteristics appear to predominate, its general chemical relations place it in this group. The oxides and acids are as follows:

Oxides	Acid
Bismuth dioxide, Bi_2O_2	Bismuthic acid, $HBiO_3$
Bismuth trioxide, Bi_2O_3	
Bismuth tetroxide, Bi_2O_4	
Bismuth pentoxide, Bi_2O_5	

83. Bismuth Dioxide.—Bismuth dioxide, Bi_2O_2, may be obtained by adding potassium hydroxide to a mixture of bismuth trichloride and stannous chloride. As stannous chloride

tends to change to stannic chloride, it acts as a reducing agent and probably takes some of the chlorine from the bismuth trichloride, forming a compound of the composition $BiCl_2$. The potassium hydroxide acting on this, precipitates bismuth dioxide, Bi_2O_2, in the form of a brown precipitate. It is obtained also by heating metallic bismuth in the air. It is a citron-yellow powder, which is stable in the air, and is insoluble in water and in the alkalies.

84. Bismuth Trioxide.—Bismuth trioxide, Bi_2O_3, is the principal oxide of bismuth and is formed when bismuth is burned in air or oxygen. It may also be prepared by igniting the nitrate, $Bi(NO_3)_3$, at a high temperature. It is a yellow powder, with basic properties. Bismuth tetroxide, Bi_2O_4, is a reddish-yellow powder of which little is known.

85. When chlorine is led through a concentrated solution of potassium hydroxide in which bismuth trioxide is suspended, bismuthic acid, $HBiO_3$, is precipitated; when gently heated this yields bismuth pentoxide, Bi_2O_5. Some experimenters claim to have obtained salts of bismuthic acid such, for example, as $NaBiO_3$, while others have failed. At all events, the acid properties of bismuthic acid and of the pentoxide, are very weak.

86. Bismuthic Acid.—Bismuthic acid, $HBiO_3$, as stated above, is obtained by passing chlorine through a concentrated solution of potassium hydroxide, in which bismuth trioxide is suspended. It may act as a very weak acid toward strong bases, but its general character is rather basic. It is a scarlet-red powder which at 120° C. gives up its water, forming the pentoxide.

BISMUTH AND CHLORINE

87. Bismuth forms two compounds with chlorine, namely: $BiCl_3$ and $BiCl_2$. The trichloride is the principal one. It may be formed by the direct action of chlorine on bismuth. It is a white, granular, deliquescent substance, fusible at 227° C. and volatile at 435° C. By contact with water it is decomposed,

forming bismuthyl chloride, $BiOCl$, also known as bismuth oxychloride.

The trifluoride, tribromide, and tri-iodide are similarly prepared and in presence of water yield precipitates of basic salts.

BISMUTH AND SULPHUR

88. Bismuth Trisulphide.—Bismuth trisulphide, Bi_2S_3, occurs in nature as bismuthinite. It is obtained as a black precipitate on adding hydrogen sulphide to solutions of bismuth; but, unlike the sulphides of arsenic and antimony, it is not soluble in solutions of the alkali sulphides. Salts called suphobismuthites are formed when combination takes place between Bi_2S_3 and a metallic sulphide. Some of these occur in nature, as, for example, lead sulphobismuthite, or kobellite, $Pb_3(BiS_3)_2$; sulphobismuthite of copper, or emplectite, $Cu(BiS_2)_2$; wittichenite, $Cu(BiS_3)_2$.

SALTS OF BISMUTH

89. By treating a solution of bismuth nitrate, $Bi(NO_3)_3$, with a cold solution of potassium hydroxide a precipitate of bismuth hydroxide, $Bi(OH)_3$, is obtained. If this is dried at 100° C. water is driven off, and the hydroxide $BiOOH$ results. The salts of bismuth are derived from these two hydroxides. The salts derived from the triacid base, $Bi(OH)_3$, are known as bismuth salts, and those derived from the monacid base, $BiOOH$, are called bismuthyl salts. The most common salts of bismuth are the sulphates and nitrates. By dissolving bismuth trioxide in dilute sulphuric acid, acid bismuth sulphate, $BiH(SO_4)_2$, is obtained. This compound is not as stable, however, as bismuthyl sulphate, $(BiO)_2SO_4$. Bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$, is obtained by dissolving bismuth in nitric acid and evaporating to dryness. Water decomposes this salt, forming basic nitrates, the composition of which depends on a number of circumstances, as, for example, the quantity and temperature of the water, the amount of free acid present, etc.

Among the best known basic nitrates of bismuth are: $BiONO_3$, $Bi(OH)_2ONO_2$, and $(BiO)_2OHONO_2$.

There are many others, however, that are more complex in composition.

REVIEW OF THE NITROGEN-PHOSPHORUS GROUP

90. From a study of the properties of the nitrogen-phosphorus group of elements, a gradual transition from the so-called non-metals to the metals is noted. Nitrogen and phosphorus, which head the group, are non-metallic. Arsenic, which comes third, is the first to exhibit those properties, such as luster and high specific gravity, which are the common properties of the metals. The element antimony exhibits still more of those properties common to metals than does arsenic, and by its physical appearance it could not be distinguished from a true metal. Bismuth, the last member of the family, physically, at least, possesses no non-metallic properties.

91. All of the elements of this family form oxides, the most important of which, for comparative purposes, are the trioxides and the pentoxides. The oxides of nitrogen and phosphorus are acidic in character and are anhydrides of acids. With arsenic trioxide, the first indication of basicity is met with and halogen salts of arsenic are formed by the interaction of the trioxide and halogen acids. The solution of the trioxide in hot water, however, gives rise to arsenious acid. The pentoxide has no basic properties.

92. The trioxide of antimony is both base-forming and acid-forming. Thus, an aqueous solution is neutral to litmus, while antimony sulphate, $Sb_2(SO_4)_3$, and antimony nitrate, $Sb(NO_3)_3$, are formed by the action of sulphuric and nitric acids on the trioxide. The aqueous solution of antimony pentoxide reddens blue litmus and possesses no basic properties. Bismuth trioxide is strongly basic and dissolves in acids to form salts. The pentoxide acts similarly.

93. It is evident from the preceding that the acidic character of the oxides of the elements of the nitrogen-phosphorus

group diminishes with the transition from nitrogen to bismuth, and it may be added that the strength of the oxygen acids which these elements form, namely, nitric, phosphoric, arsenic, antimonic, and bismuthic, also diminishes from nitric to bismuthic.

Of the five elements constituting the nitrogen-phosphorus group, four unite with hydrogen; bismuth does not. Of these four, nitrogen combines directly with hydrogen, while phosphorus, arsenic, and antimony form hydrides indirectly. Ammonia possesses strong basic properties, phosphine is a feeble base, while arsine and stibine do not exhibit basic properties.

94. All of the elements of this group unite with chlorine, the stability of the chlorides formed increasing in passing from nitrogen trichloride to bismuth trichloride. The boiling points of the halogen compounds increase with the increasing atomic weight; thus, NCl_3 has a boiling point of 71°; PCl_3, 76°; $AsCl_3$, 130.2°; $SbCl_3$, 223.5°, and $BiCl_3$, 447°.

The practical uses to which the periodic law and table can be put become evident when studying the chemistry of a group of elements such as the halogens, the nitrogen-phosphorus family, and other groups which follow.

When the closely related members of a group are known, in many instances it will be found that a knowledge of the properties of one element of the group will help greatly to obtain a clear idea of the chemical behavior and physical properties of the other members of the group.

VANADIUM GROUP

CLASSIFICATION

95. The vanadium group consists of the rare elements, vanadium; columbium, or niobium; tantalum; praseodymium, or didymium; and neodymium, all of which are rather closely related to the nitrogen-phosphorus group of elements.

Vanadium has probably been studied more thoroughly than any of the others because of the practical use which has been found for it. Comparatively little is known of the other elements of this group.

VANADIUM

Symbol V. Atomic weight 51

96. History.—Vanadium was discovered in 1801 by Del Rio in a lead ore (vanadinite) obtained in Mexico. He called the new metal *erythronium* from the Greek meaning *red*, because, being treated with acids, a red product was formed. In 1805, however, Collet-Descotils stated that the newly discovered metal was an impure oxide of chromium, and no further work on his discovery was done by Del Rio.

97. In 1830 Sefström discovered a new metal while working with Swedish iron ores. He called this new metal vanadium after the Scandinavian goddess Vanadis. Shortly after Sefström's discovery it was shown by Wöhler that the erythronium of Del Rio was identical with Sefström's vanadium. At the request of Sefström, the investigation of the new metal was carried out by Berzelius, who, as was shown by Roscoe in 1867, mistook the oxide of the metal for the metal itself and concluded that it possessed properties similar to those of chromium and molybdenum. In 1867, however, it was shown

conclusively by Roscoe that metallic vanadium was closely related to the nitrogen-phosphorus group of elements.

98. Occurrence.—Vanadium occurs in nature in the form of vanadates, which are analogous to phosphates. It has been found in clay, coal, and some rare minerals. Its principal minerals are vanadinite, $3Pb_3V_2O_5 \cdot PbCl_2$; dechenite, $PbVO_3 \cdot ZnVO_3$; descloizite, $Pb_2V_2O_7$; mottramite, $(CuPb)_5V_2O_{10} \cdot 2H_2O$, and carnotite, $K_2O2UO_3V_2O_53H_2O$, which is found in Colorado.

99. Preparation.—Metallic vanadium is never prepared on a large scale for industrial purposes, and the preparation of even small quantities of the pure metal in the laboratory is a difficult undertaking. It may be prepared, however, by reducing anhydrous vanadium dichloride, VCl_2, in pure hydrogen. The oxide, V_2O_5, is prepared by first digesting the ore with hydrochloric or nitric acid and then filtering off the acid solution. The residue is well washed with water. This solution, together with the washings, is evaporated with an excess of ammonium chloride, when ammonium metavanadate, NH_4VO_3, is precipitated; this is then purified by crystallization. The ammonium metavanadate is then gently roasted, forming vanadium pentoxide.

100. Another method is to fuse the ore with potassium nitrate, converting the vanadium into potassium vanadate, K_3VO_4. A salt of lead or barium is added to the solution of potassium vanadate and the precipitate obtained is decomposed with sulphuric acid. The vanadic acid formed is neutralized with ammonium hydroxide and the ammonium vanadate precipitated by means of ammonium chloride, in which it is insoluble. This is then converted by ignition into the pentoxide. An impure vanadium can now be prepared by reducing the oxide with carbon in the electric furnace.

101. The impure metal thus produced is then converted to the tetrachloride, VCl_4, by the action of an excess of dry chlorine. The dichloride is then obtained from the tetrachloride by reducing the latter in a stream of hydrogen.

102. Properties.—Vanadium is a grayish-white, nonmagnetic powder having a specific gravity of 6.025 at 15° C., and melting in an atmosphere of hydrogen at 1,720° C. Heated in oxygen, it burns with a brilliant display of sparks, forming the oxide. The metal is insoluble in hydrochloric acid and in cold sulphuric acid. Hot concentrated sulphuric acid slowly attacks it, however. The metal is also soluble in hydrofluoric acid; any strength of nitric acid attacks it violently. Metallic vanadium precipitates silver, gold, and platinum from solutions of their salts. When metallic vanadium is heated in an atmosphere of pure nitrogen, the mononitride, VN, is formed.

103. Uses of Vanadium.—The reason why vanadium has been more thoroughly investigated than its companions in this group of elements is because of its great value in the manufacture of steel.

104. As stated previously, under the discussion of the preparation of this metal, very little is prepared in the pure state, but nearly 5,000 tons of ferrovanadium, an alloy of vanadium with iron containing between 35 and 40 per cent. vanadium, are used annually in the manufacture of steel. When added to molten steel in quantities of .25 to 1.50 per cent., vanadium forms an alloy and also acts as a scavenger, as it is claimed that it removes occluded nitrogen and oxygen.

105. When added to steel in small quantities (.10 to .30 per cent.), vanadium imparts a great toughness and strength to the product and is, therefore, used in steels which go into automobile axles and frames and into those parts which are subjected to severe vibration. Large quantities are also used in the manufacture of tool and high-speed steels; smaller quantities are used in the manufacture of inks, medicines, and dyes.

COMPOUNDS OF VANADIUM

106. Vanadium and Oxygen.—With oxygen, vanadium forms five compounds which recall the oxygen compounds of nitrogen. They are: suboxide, V_2O; dioxide, V_2O_2; triox-

ide, V_2O_3; tetroxide, V_2O_4, and pentoxide, V_2O_5. The acids of vanadium which are known are metavanadic, HVO_3; pyrovanadic, $H_4V_2O_7$, and hexavanadic, $H_4V_6O_{17}$. Normal, or orthovanadic, acid, H_3VO_4, is unknown, but salts of this acid have been obtained. The salts of the vanadic acids are similar in structure to those of the acids of phosphorus. Ammonium metavanadate, NH_4VO_3, is the most important vanadate.

107. Vanadium and the Halogens.—With chlorine, vanadium forms the tetrachloride, VCl_4; trichloride, VCl_3; and the dichloride, VCl_2. With fluorine, only the trifluoride is formed, $VF_3 \cdot HO_2$. Only one bromide and no iodides have been identified. The known compound with bromine is the tribromide, VBr_3.

108. The compounds, vanadium oxydifluoride, VOF_2; vanadium oxytrichloride, $VOCl_3$; oxydichloride, $VOCl_2$; and oxymonochloride, $VOCl$, and other oxygen compounds of chlorine are known. The oxygen compounds with bromine and iodine are: vanadyl tribromide, $VOBr_3$, and divanadyl tetraiodide, $V_2O_2I_4 \cdot 8H_2O$.

COLUMBIUM

Symbol Cb. Atomic weight 93.1

109. Occurrence, Preparation, and Properties. Columbium, which is also sometimes called niobium, is found principally in the mineral columbite, though it also occurs in euxenite, pyrochlore, and some other rare minerals. It may be obtained by passing the vapor of columbium chloride mixed with hydrogen, through a red-hot tube. It is a steel-gray element having a metallic luster and a specific gravity of 7.1. When ignited in the air, it burns readily to the pentoxide. It is insoluble in hydrochloric, nitric, or nitrohydrochloric acid, but is soluble in hot sulphuric acid.

110. Compounds of Columbium.—There are three oxides of columbium, Cb_2O_2, Cb_2O_4, and Cb_2O_5. The pentoxide, Cb_2O_5, may be reduced to the tetroxide, Cb_2O_4, by heat-

ing it strongly in hydrogen, but when this is heated in the air it is again oxidized to the pentoxide. With chlorine, columbium forms two compounds, $CbCl_3$ and $CbCl_5$.

A bromide having the formula $CbBr_5$, and a fluoride, CbF_5, are known. The fluoride combines with fluorides of other metals, forming fluocolumbates of the general form M_2CbF_7. The columbates are derived from a number of forms of the acid, all of which are closely related to the ortho-acid, H_3CbO_4.

TANTALUM

Symbol Ta. Atomic weight 181.5

111. Occurrence and Preparation.—Tantalum occurs in nature in the minerals columbite, tantalite, and some other rare minerals. It obtained its name from the difficulty of separating it from its combinations. Berzelius prepared it by heating potassium fluotantalate with potassium, but Von Bolton obtained it pure by heating the product obtained as did Berzelius, in an electric furnace in a vacuum. It is a silver-white metal as hard as steel, ductile and malleable when hot; its specific gravity is 16.6, and its melting point is 2,250° C.

112. Compounds of Tantalum.—There are two oxides of tantalum, Ta_2O_4 and Ta_2O_5. With the halogens it forms the penta compounds, TaF_5, $TaCl_5$, $TaBr_5$, and TaI_5. Tantalum fluoride unites readily with fluorides of the other metals, forming fluotantalates of the general formula M_2TaF_7. Thus, by treating tantalum fluoride with a solution of potassium fluoride, potassium fluotantalate, K_2TaF_7, is obtained.

The tantalates are derived from metatantalic acid, $HTaO_3$, or hexatantalic acid, $H_8Ta_6O_{19}$, both of which appear to be derived from orthotantalic acid, H_3TaO_4, by the loss of water.

PRASEODYMIUM

Symbol Pr. Atomic weight 140.9

113. Occurrence and Preparation.—At one time the substance known as didymium was supposed to be an element. This substance was found in cerite and in monazite sand. It was separated from cerium and lanthanum by Mosander in 1840 and by him reported as an element. Welsbach in 1885 by making several thousand fractionations of didymium nitrate, obtained a pale-green salt and a rose-colored salt, which gave different spectra from the original salt, but which when united gave the spectrum of didymium. Praseodymium may be prepared by the electrolysis of the chloride. It has a yellow color, melts at 940° C., has a specific gravity of 6.5, and is unaffected by air.

114. Compounds of Praseodymium.—A dioxide, PrO_2, and a trioxide, or sesquioxide, Pr_2O_3, are known. The dioxide, PrO_2, is obtained as a black powder by heating a mixture of the nitrate with potassium nitrate to about 425° C. The sesquioxide, Pr_2O_3, is obtained as a light green powder by heating the dioxide in hydrogen. Praseodymium also forms a hydroxide, $Pr(OH)_3$; a chloride, $PrCl_3$; a sulphate, $Pr(SO_4)_3$; and a nitrate, $Pr(NO_3)_3$. The hydroxide is a pale-green powder, whereas the remaining compounds form pale-green crystalline salts.

NEODYMIUM

Symbol Nd. Atomic weight 144.3

115. Neodymium salts occur with samarium salts and are separated from the latter by fractional precipitation. It has a yellow color, melts at 840° C., and is slowly acted on by the air. Its chemical properties resemble very closely those of praseodymium. It has a specific gravity of 6.95. One stable oxide, the sesquioxide, Nd_2O_3, and an unstable dioxide, NdO_2, are known. The salts of neodymium are prepared from the sesquioxide and are rose colored.

INORGANIC CHEMISTRY
(PART 9)

THE ALKALIES AND THEIR COMPOUNDS

INTRODUCTORY

1. The division of the elements into metals and non-metals was at first based on physical properties. The elements that possessed metallic luster, were opaque, and were good conductors of heat and electricity were known as metals; the elements that did not possess these properties, or possessed them in a much less marked degree, were classed as non-metals. Gradually, however, the chemical character of the element became the chief factor in deciding to which class it belonged, until at present the principal consideration in deciding whether an element shall be classed as a metal or non-metal is whether its oxides and hydroxides are acidic or basic. If the element is base forming, it is usually considered as a metal; if it is acid forming, it is classed as a non-metal. This division is not perfect, however, for some elements form both bases and acids. On this account, it is best to lay less stress on the classification as metals and non-metals, and base our classification on the natural division, known as the periodic system. Though this system has been followed in the preceding Sections, it will be noticed that the list of elements already treated very nearly coincides with the list of elements usually treated as non-metals, while those that remain to be treated are nearly identical with those usually classed as metals.

2. The metals usually occur in nature in the form of compounds called ores, their extraction from which has grown into a science known as metallurgy. It would be impossible in a work of this character to give a complete description of all the processes for the preparation of the metals, and consequently only those that best illustrate the chemical principles involved will be given.

The chemical activity of those elements already studied varies inversely with the atomic weight; that is, the element having the lowest atomic weight is the most active. For example, the oxides of nitrogen are strongly acidic, those of phosphorus and arsenic less so, while those of bismuth seem to be basic rather than acidic. The same thing is generally true of the metals. The lighter members of a group are the most active chemically, while the heavier ones are much less active. As a rule, the lighter metals form strong bases, while the heavier ones form weak bases and in some cases act also as acid-forming elements.

3. The Alkalies.—The alkali group consists of the elements potassium, sodium, lithium, rubidium, and cæsium, and the compound, ammonium. The elements are all soft metals having a silvery luster, and are easily melted and volatilized. As their atomic weights become greater, their melting and boiling points become lower, and their specific gravities become higher. Of all the metals they are the most strongly electropositive. Of these, sodium and potassium are most abundant, lithium is not nearly so common, and rubidium and cæsium are quite rare. The hydroxides of these metals are soluble in water, and are the strongest bases known; they unite with all acids, forming salts that are as a rule very stable. The members of this group act as monovalent elements. As potassium and sodium are the most abundant and important members of this group, they will be treated first.

POTASSIUM

Symbol K, Atomic weight 39.1

4. History and Occurrence.—The discovery of potassium dates back to 1807, when Sir Humphry Davy obtained this metal by submitting potassium hydroxide to electrolysis; soon after, Gay-Lussac and Thenard prepared it chemically in the pure state. Though rather abundant in nature, it is found only in combination and never pure. In the mineral kingdom it occurs as nitrate or saltpeter, as chloride or sylvite, as potassium-magnesium chloride or carnallite, and as sulphate or aphthitalite. It is also found in various combinations in the waters of the ocean and in mineral springs as well as in land plants, and it appears to be essential to animal life.

5. Preparation.—Metallic potassium may be prepared by heating a mixture of potassium carbonate and carbon to a high temperature; thus,

$$K_2CO_3+2C+\text{heat}=3CO+2K$$

The mixture is heated to a white heat in an iron retort and the vapors are passed into a copper receiver. The potassium distils over and condenses in globules, still containing carbon in the form of charcoal. It is purified by redistillation in an iron retort and is condensed in a copper receiver filled with naphtha.

The manufacture of potassium is rather dangerous, owing to the formation of a very explosive compound of potassium and carbon monoxide, called potassium carbonyl, which has the probable composition, $K_2(CO)_2$. It has been proposed to manufacture potassium by heating the hydroxide, KOH, with magnesium, the potassium distilling off in the current of evolved hydrogen:

$$2KOH+2Mg=2MgO+2K+H_2$$

In later years, probably most of the metallic potassium manufactured has been prepared by the electrolysis of the fused chloride, KCl, or a fused mixture of potassium chloride and calcium chloride.

Potassium may also be prepared by the electrolytic methods subsequently described under the preparation of metallic sodium.

6. Properties.—Potassium is a soft, brilliant, bluish-white metal, which tarnishes instantly, however, in the air to a dull grayish color. Because of its great chemical activity, it must always be kept from contact with air or moisture, and for this reason it is always preserved under naphtha, kerosene, and similar liquids. It possesses a specific gravity of .862 at 20° C., becomes brittle at 0° C., and melts at 63.5° to a liquid closely resembling mercury. When heated to about 757° C., potassium boils.

When put in water, potassium at once decomposes it, evolving so much heat that the hydrogen which has been set free takes fire and burns with a characteristic violet flame. It unites actively with chlorine and with sulphur. Its spectrum is characterized by two sharply defined lines—one in the red, having a wave length of .000768 millimeter, and the other in the violet, having a wave length of .0004045 millimeter. As minute a quantity of potassium as $\frac{1}{3000}$ milligram may be detected with absolute certainty, by means of this spectrum.

POTASSIUM OXIDES

7. Potassium Oxide.—Potassium oxide, K_2O, is obtained by the direct oxidation of the metal, as when it is burned in air or oxygen and the product is ignited, or when potassium hydroxide is heated with potassium, according to the equation:

$$2KOH+2K=2K_2O+H_2$$

It is a grayish-white, deliquescent, caustic substance, and unites energetically with water to again form the hydroxide.

8. Potassium Peroxide, or Tetroxide.—Potassium peroxide, K_2O_4, is formed when potassium is heated with an excess of oxygen.

$$2K+2O_2=K_2O_4$$

It is a yellow powder which at white heat breaks up into potassium oxide and oxygen. On treatment with water, potassium hydroxide and hydrogen peroxide are formed and oxygen is set free.

$$K_2O_4+2H_2O=2KOH+H_2O_2+O_2$$

It is a strong oxidizing agent.

9. Potassium Hydroxide, or Caustic Potash. Potassium hydroxide, *KOH,* is also called caustic potash and potassium hydrate. It may be prepared by adding milk of lime, or slaked lime, $Ca(OH)_2$, to a dilute boiling solution of potassium carbonate. Thus,

$$\underset{\substack{\text{potassium}\\ \text{carbonate}}}{K_2CO_3} + \underset{\substack{\text{calcium}\\ \text{hydroxide}}}{Ca(OH)_2} = \underset{\substack{\text{calcium}\\ \text{carbonate}}}{CaCO_3} + \underset{\substack{\text{potassium}\\ \text{hydroxide}}}{2KOH}$$

The calcium combines with the carbonic acid, forming insoluble calcium carbonate, while the potassium hydroxide remains in solution.

When the reaction has gone to completion (determined by testing a portion of the clear solution with *HCl,* the absence of effervescence indicating completion) the liquid is allowed to settle and the clear solution is decanted and rapidly evaporated. The residue is melted and poured out on flat stone slabs. This product is impure and by treating it with alcohol, which dissolves only the potassium hydroxide, it may be freed of lime and any salts of potassium it may possess—especially of the carbonate, which is formed by the absorption of carbon dioxide. The clear alcoholic solution is decanted and after the alcohol has been expelled by distillation the residue is evaporated to dryness and fused.

10. Potassium hydroxide is frequently prepared also by the electrolysis of a solution of potassium chloride.

Freshly fused potassium hydroxide occurs as opaque, white fragments having a short fibrous fracture. It melts just below a red heat to an oily liquid and volatilizes at a white heat; it is not decomposed by heat. When exposed to the air, it absorbs moisture as well as carbon dioxide from the atmosphere, and deliquesces. It is very soluble in water.

Potassium hydroxide is very caustic; it softens and partly destroys the skin, and is for this reason employed as a caustic in surgery. It shows the properties of an alkali in the highest degree; these are its solubility in water, its power to neutralize the acids and to decompose a great number of metallic solutions, and its corrosive action on the tissues. This alkalinity may be shown by the energy with which the most dilute solutions of potassium hydroxide restore the blue color to reddened litmus.

SULPHIDES OF POTASSIUM

11. Potassium Sulphide.—Potassium sulphide, K_2S, is obtained by passing hydrogen over heated potassium sulphate or by gently heating a mixture of potassium sulphate and carbon; thus:

(1) $$K_2SO_4+4H_2=K_2S+4H_2O$$

(2) $$K_2SO_4+2C=K_2S+2CO_2$$

The sulphide obtained by using hydrogen is a red, crystalline mass, whereas a flesh-colored porous mass is obtained when carbon is used. A solution of the sulphide can be obtained by saturating a solution of potassium hydroxide with hydrogen sulphide and adding an equal quantity of the hydroxide. If the sulphide is fused it solidifies in a red, crystalline mass which is deliquescent in moist air and is soluble in water.

12. Potassium Hydrosulphide.—Potassium hydrosulphide, KSH, may be prepared by treating potassium carbonate heated to dull redness with hydrogen sulphide as shown in the equation:

$$K_2CO_3+2H_2S=2KSH+H_2O+CO_2$$

It forms a white or yellow deliquescent solid which is very soluble in water. When exposed to the air, its aqueous solution becomes yellow from the formation of the disulphide; thus:

$$4KSH+O_2=2K_2S_2+2H_2O$$

If exposed for a longer time the solution becomes colorless, potassium thiosulphate being formed; thus:

$$2K_2S_2+3O_2=2K_2S_2O_3$$

POTASSIUM AND CHLORINE

13. Potassium Chloride.—Potassium chloride, KCl, constitutes the mineral sylvite, and closely resembles rock salt. It is obtained commercially from sea-water, from kelp (the ash of seaweed), from the refuse of the manufacture of beet root sugar, or from an abundant mineral of the Stassfurt mines, carnallite, which is potassium-magnesium chloride. It is a transparent, colorless solid that crystallizes in cubes; it has a specific gravity of 1.98 and a bitter, salty taste. It is soluble in water and in dissolving produces a lowering of temperature. One part of potassium chloride dissolves in 3 parts of water at 17.5° C., and 100 grams of water at 0° C. dissolves 28.5 grams of potassium chloride.

POTASSIUM AND IODINE

14. Potassium Iodide and Bromide.—Potassium iodide and bromide are commercially important on account of their use in medicine and photography.

Potassium iodide, KI, is prepared on a large scale by the direct action of iodine on potassium hydroxide:

$$\underset{\text{iodine}}{3I_2} + \underset{\substack{\text{potassium}\\\text{hydroxide}}}{6KOH} = \underset{\substack{\text{potassium}\\\text{iodide}}}{5KI} + \underset{\substack{\text{potassium}\\\text{iodate}}}{KIO_3} + \underset{\text{water}}{3H_2O}$$

Potassium iodide and iodate are formed, the latter being precipitated. The whole is evaporated to dryness and the residue heated to redness with powdered charcoal, whereby the iodate is converted into iodide. The mass is dissolved in hot water; on cooling, the solution deposits the iodide in fine, colorless, transparent cubes. One hundred parts of water at 18° C. dissolves 143 parts of potassium iodide; it is also readily soluble in alcohol. A solution of potassium iodide dissolves iodine readily.

Potassium bromide, KBr, is similar in properties to the iodide and is obtained by an analogous process. It crystallizes in cubes that are soluble in about 1.5 parts of cold water.

SALTS OF POTASSIUM

15. Potassium Nitrate.—Potassium nitrate, KNO_3, long known as saltpeter, or niter, is found in parts of India, in Egypt, Persia, Hungary, Spain, etc., where it sometimes appears as a white incrustation on the surface of the soil and is sometimes mixed with the soil to some depth. The saltpeter is extracted from the earth by digesting the latter with water; the solution is decanted from the insoluble residue and then evaporated, first by the heat of the sun and afterwards by artificial heat. Upon cooling the concentrated solution thus obtained, impure crystals are formed, which are exported as grough (or impure) saltpeter. It is far less abundant in northern climates than in southern. It is formed wherever nitrogenized organic substances decompose in the presence of potassium hydroxide, and is manufactured artificially by exposing to the air mixtures of animal matter with wood ashes and lime moistened with stable drainings or stale urine. The greater part of the saltpeter of commerce is now obtained from sodium nitrate, of which enormous deposits occur in Peru and Chile.

16. The conversion of this so-called Chile saltpeter, or impure sodium nitrate, into potassium nitrate is effected in the following manner: The recrystallized sodium nitrate is dissolved in water, and an equivalent quantity of potassium chloride which is abundantly obtained from the Stassfurt mines, is added, when a double decomposition takes place. The solution is boiled down; the hot liquid deposits sodium chloride, which is separated, and potassium nitrate crystallizes out on cooling.

Potassium nitrate crystallizes from its aqueous solution in long, six-sided prisms that have a cool and slightly bitter taste. It melts at 337° C.; at a higher temperature it disengages oxygen and is converted into potassium nitrite, KNO_2, which in its turn is decomposed at a red heat, leaving a mixture of oxide and peroxide of potassium. Potassium nitrate is very soluble in water, the solvent power of the water increas-

ing as its temperature rises. While 100 parts of water at 0° C. dissolves only 13.33 parts of potassium nitrate, at 100° C. it dissolves 246 parts. Potassium nitrate is used largely in the manufacture of gunpowder, which is an intimate mixture of niter, charcoal, and sulphur.

17. Potassium Sulphate.—Potassium sulphate, K_2SO_4, is found in certain salt mines in the mineral kainite, $K_2SO_4{\cdot}MgSO_4{\cdot}MgCl_2{\cdot}6H_2O$. It is also largely obtained as a secondary product in various manufacturing processes. It is obtained as the result of the reaction between potassium carbonate and the acid potassium sulphate that is formed in the preparation of nitric acid by the decomposition of potassium nitrate with sulphuric acid.

$$K_2CO_3+2KHSO_4=2K_2SO_4+CO_2+H_2O$$

Potassium sulphate is prepared also by the action of concentrated sulphuric acid on potassium chloride. Potassium sulphate melts at 1,072° C., is soluble in about 10 parts of cold water, but in a much smaller quantity of boiling water. It has a bitter taste and is neutral to test paper. Its crystals are a combination of rhombic pyramids and prisms resembling in formation and appearance those of quartz. They are anhydrous and decrepitate when suddenly heated, which is often the case with anhydrous crystals, that is, those that contain no water of crystallization. They are insoluble in alcohol.

18. Acid Potassium Sulphate.—Acid potassium sulphate, $KHSO_4$, commonly known as potassium bisulphate, may be prepared by mixing potassium sulphate with half its weight of concentrated sulphuric acid, and evaporating the mixture to dryness in a platinum vessel; the residue is then treated with just enough hot water to dissolve it, and left to crystallize. The crystals melt at about 200° C., losing water and being converted into the pyrosulphate, $K_2S_2O_7$. They are much more soluble than the normal salt, 36 parts dissolving in 100 parts of water at 0° C., and 121 parts in 100 parts of boiling water. The solution is acid to litmus and has a sour taste.

19. Potassium Chlorate.—Potassium chlorate, $KClO_3$, may be prepared by passing chlorine into a hot (70° C.), aqueous solution of potassium hydroxide; thus:

$$3Cl_2+6KOH=KClO_3+5KCl+3H_2O$$

Until recently, potassium chlorate was produced on a commercial scale by a process involving the action of chlorine on a mixture of slaked lime, potassium chloride, and water which have been heated in closed vessels. Chlorate and chloride of calcium are formed:

$$6Ca(OH)_2+6Cl_2=Ca(ClO_3)_2+5CaCl_2+6H_2O$$

and in the presence of the potassium chloride a double decomposition takes place, potassium chlorate and calcium chloride, which latter is very soluble, being formed. Thus:

$$Ca(ClO_3)_2+2KCl=2KClO_3+CaCl_2$$

The solution is filtered hot and upon cooling the less soluble potassium chlorate crystallizes out.

20. This method is now being replaced by the electrolytic method, according to which hot solutions of potassium chloride are electrolyzed; the intermediate steps of the reaction which takes place are in doubt, but chlorine is first formed, then potassium hypochlorite, and finally potassium chlorate. The reaction may be summed up as follows:

$$KCl+3H_2O=KClO_3+3H_2$$

Potassium chlorate melts at 357° C., and at a higher temperature is decomposed into oxygen, potassium perchlorate, and potassium chloride. Potassium chlorate deflagrates when strongly heated; when mixed with sulphur, it explodes by friction or percussion. It is a powerful oxidizing agent.

21. Potassium Carbonate.—Potassium carbonate, K_2CO_3, is met in commerce in the impure condition under the name potash. It is obtained by lixiviating wood ashes; that is, digesting them with water, filtering, evaporating the solution to dryness, and calcining the residue in the air. The potash thus obtained is impure potassium carbonate mixed with various other salts of potassium such as the chloride and sulphate and silicate, and contains approximately only from 60 to 80 per

cent. of carbonate. Potassium carbonate is now manufactured on a large scale from the native chloride, so-called Stassfurt salt, by a process similar to that subsequently described for the manufacture of sodium carbonate from common salt.

Potassium carbonate is found also in the wool of sheep. The liquors obtained from the washing of the wool are evaporated to dryness and the residue is burned in retorts.

22. Pure potassium carbonate forms a white granular powder or a white solid mass very soluble in water; it has a strong alkaline reaction and a slightly caustic taste. It is insoluble in alcohol. It melts at 909° C. and volatilizes at a white heat. It absorbs moisture readily from the air. Potassium carbonate is largely employed for various purposes in the industries and is a compound of considerable importance.

23. Acid Potassium Carbonate.—Acid potassium carbonate, $KHCO_3$, or potassium bicarbonate, being much less soluble than the normal salt, crystallizes out of solution when a concentrated solution of the normal salt is treated with carbon dioxide; thus:

$$K_2CO_3+H_2O+CO_2=2KHCO_3$$

It is prepared also by passing carbon dioxide over moist potassium carbonate and recrystallizing the product from warm water. It crystallizes in large transparent monoclinic prisms without water of crystallization. It has a salty taste and an alkaline reaction. By heating to 190° C., or by boiling the aqueous solution, carbon dioxide is evolved and water is given off with the formation of the normal salt, according to the equation:

$$2KHCO_3=K_2CO_3+H_2O+CO_2$$

24. Potassium Phosphates.—Potassium orthophosphate, K_3PO_4, is formed by igniting phosphoric acid with excess of potassium carbonate. Thus,

$$3K_2CO_3+2H_3PO_4+\text{heat}=2K_3PO_4+3CO_2+3H_2O$$

It is readily soluble in water and crystallizes in small needles. The secondary salt, K_2HPO_4, is obtained by mixing aqueous phosphoric acid with a quantity of carbonate of potassium

sufficient to produce a slight alkaline reaction, and evaporating. This salt is easily soluble in water, but it does not crystallize. The reaction is as follows:

$$K_2CO_3+H_3PO_4+H_2O=K_2HPO_4+CO_2+2H_2O$$

The primary salt, KH_2PO_4, obtained by using a slight excess of phosphoric acid forms small needle-shaped crystals which are easily soluble in water but insoluble in alcohol. It is used in artificial fertilizers. The reaction between the carbonate and the acid is as follows:

$$K_2CO_3+2H_3PO_4=2KH_2PO_4+CO_2+H_2O$$

Potassium pyrophosphate, $K_4P_2O_7$, is deliquescent and separates from aqueous solutions in fibrous crystals. It is formed by the heating of the secondary orthophosphate,

$$2K_2HPO_4+\text{heat}=K_4P_2O_7+H_2O$$

Potassium metaphosphate, KPO_3, is formed by heating the primary phosphate,

$$KH_2PO_4+\text{heat}=KPO_3+H_2O$$

This salt is almost insoluble in water; the dimetaphosphate, $K_2P_2O_6{\cdot}H_2O$, prepared by decomposing the corresponding copper salt with potassium sulphide, is soluble in water and crystallizable; it is converted by ignition into the monometaphosphate. Thus,

$$CuP_2O_6+K_2S=CuS+K_2P_2O_6$$
$$K_2P_2O_6+\text{heat}=2KPO_3$$

25. Potassium Arsenates.—The neutral salt, K_3AsO_4, is obtained by treating arsenic acid with an excess of potassium carbonate. The secondary salt, K_2HAsO_4, is crystallized with difficulty. The primary salt, KH_2AsO_4, forms large crystals.

26. Potassium Arsenites.—The salt, $KH_3As_2O_5$, is obtained as a crystalline powder on adding alcohol to a solution of arsenious oxide in the minimum quantity of potassium carbonate. When heated with a solution of potassium carbonate, it is converted into the meta-arsenite, $KAsO_2$; thus,

$$KH_3As_2O_5+K_2CO_3=2KAsO_2+KHCO_3+H_2O$$

This salt, in turn, when heated with potassium hydroxide, yields the diarsenite, $K_4As_2O_5$,

$$2KAsO_2+2KOH=K_4As_2O_5+H_2O$$

27. Potassium Borates.—The metaborate, $K_2B_2O_4$, is obtained by fusing a mixture of boric acid, H_3BO_3, and potassium carbonate,

$$2H_3BO_3+K_2CO_3=K_2B_2O_4+3H_2O+CO_2$$

is only slightly soluble in water and separates in small monoclinic crystals. It has an alkaline reaction and absorbs carbon dioxide from the air, which converts it into the pyroborate or tetraborate, $K_2B_4O_7$. Thus,

$$2K_2B_2O_4+CO_2=K_2B_4O_7+K_2CO_3$$

This latter, which is also formed on mixing a solution of boric acid with a slight excess of potassium carbonate, is easily soluble and crystallizes in hexagonal prisms containing $5H_2O$.

The triborate, $2KB_3O_5{\cdot}5H_2O$, is formed on mixing the hot solution of boric acid and potassium carbonate and separates in rhombic crystals,

$$6H_3BO_3+K_2CO_3=2KB_3O_5+9H_2O+CO_2$$

The pentaborate, $KB_5O_8{\cdot}4H_2O$, separates in rhombic octahedrons from a hot solution of potassium hydroxide saturated with boric acid,

$$5H_3BO_3+KOH=KB_5O_8+8H_2O$$

28. Potassium Silicate.—A silicate of potassium is formed when silica, SiO_2, is fused with potassium carbonate. Its composition appears to vary. It is soluble in water, and on evaporating in air the solution deposits a glassy-appearing substance. It may be prepared also by dissolving silicon dioxide, SiO_2, in potassium hydroxide.

SODIUM

Symbol Na. Atomic weight 23.0

29. History and Occurrence.—Though sodium oxide was already recognized in the year 1736 by Duhamel, the metal in the pure state was not obtained until 1807 by Sir Humphry Davy. Sodium does not occur free in nature, but is found abundantly in combinations. Its chloride, or salt, is known as the mineral halite, and is found not only in immense deposits of rock salt but also in enormous quantities in sea-water and in saline springs. Sodium also occurs in the form of nitrate, or Chile saltpeter; of borate, or borax; of carbonate, or trona; and of silicate, in albite, oligoclase, sodalite, etc. It is found in marine plants and is essential to animal life.

30. Preparation and Properties.—Sodium may be prepared by distilling a mixture of sodium carbonate and carbon, when the metal distils over, according to the equation:

$$Na_2CO_3+2C=2Na+3CO$$

It has also been prepared by reducing its oxide with carbon at a white heat, thus:

$$Na_2O+C=2Na+CO$$

Practically, 30 kilograms of dry sodium carbonate, 13 kilograms of charcoal, and 3 kilograms of calcium carbonate are intimately mixed together, calcined, and introduced into iron cylinders heated in a reverberatory furnace. At a bright-red heat the sodium distills over and is collected in receivers. To purify it, it is redistilled, melted under petroleum, and cast into ingots, which are preserved under naphtha, kerosene, or similar liquids, free from water.

These processes have been almost entirely superseded by the electrolytic method. In this method fused sodium hydroxide is electrolyzed in an iron vessel or cell. The metallic sodium being lighter than the hydroxide, it rises together with the hydrogen from the negative pole and is collected in a receiver. The hydrogen escapes around the edges of the cover of the receiver. More sodium hydroxide is

added from time to time to replace the metal removed, thus making the process continuous.

31. Sodium is a lustrous, silver-white, soft metal which like potassium may be easily cut with a knife; its specific gravity is .972; it becomes brittle at $-20°$ C., melts at 97.6° C., and boils at 877.5° C. On exposure to air it tarnishes rapidly and if thrown on water, decomposes it, the action being accompanied by effervescence; if it is prevented from moving or if the water is warm, it takes fire and burns with a characteristic yellow flame. Sodium is far less costly than potassium and is used on a large scale for the extraction of the metal magnesium and for making sodium peroxide. An amalgam of sodium is also employed with advantage in extracting gold and silver from their ores.

COMPOUNDS OF SODIUM

32. Sodium chloride, $NaCl$, is common salt, or sea salt. It occurs widely diffused in nature and is found in the solid state as rock salt in many countries. Sea-water contains a large proportion of sodium chloride and it exists also in various mineral springs. It may be formed by the direct union of its constituents, as by burning sodium in chlorine gas. It is obtained commercially either by mining it directly, in which form it is known as rock salt, or by evaporating either sea-water or the waters of saline springs, producing so-called solar salt if the heat is natural, and boiled salt if artificial heat is employed. Much of the salt of commerce was formerly obtained by the evaporation of sea-water along the Mediterranean. The water is let into basins a few inches deep which are continually swept by the summer winds. The salt solution thus becomes concentrated and is passed from one basin to the next until it arrives in the areas where the salt is deposited.

33. Extensive beds of rock salt occur in Russia, France, Germany, Hungary, Spain, Abyssinia, Mexico, and various parts of the United States. Perfectly pure specimens of rock salt form beautiful, colorless cubes, and are known as

sal gemme, but ordinary rock salt is only partly transparent and exhibits a rusty color owing to the presence of iron. At Droitwich, Worcestershire, England, the salt is obtained by evaporation from the waters of saline springs. In some parts of France and Germany where the salt springs contain so little salt that it would not pay for the fuel necessary to evaporate the water, a very ingenious plan is adopted by which the proportion of water is greatly reduced without the application of artificial heat. The water is pumped to the top of a framework filled with bundles of twigs and brushwood, as shown in Fig. 1. The water, in trickling over the twigs and brushwood, exposes a large surface to the action of the wind and the sun and a considerable evaporation takes place, so that a much stronger brine is collected in the reservoir beneath the scaffolding; by several repetitions of the operation the proportion of water is so far diminished that the rest may be economically evaporated by artificial heat.

34. Sodium chloride is a colorless, transparent solid that crystallizes in cubes from its aqueous solution. The crystals are generally very small, are anhydrous, and nearly equally soluble in hot and cold water. The saturated solution boils at 109.7° C.

The great tendency of ordinary table salt to become damp when exposed to the air is due chiefly to the presence of small quantities of chlorides of magnesium and calcium, for pure sodium chloride has very little tendency to attract atmospheric moisture, although it is easily dissolved by water.

Salt is used as a refrigerating medium and for preserving meats, fish, etc.; it is also used in the manufacture of soaps, dyes, chemicals, and pottery, and salt solutions are employed in surgery.

35. Oxides of Sodium.—Sodium oxide, Na_2O, may be obtained by the combustion of sodium in air and heating the product thus obtained, with sodium; it is a white, fusible substance, uniting directly with water to form sodium hydroxide, $NaOH$.

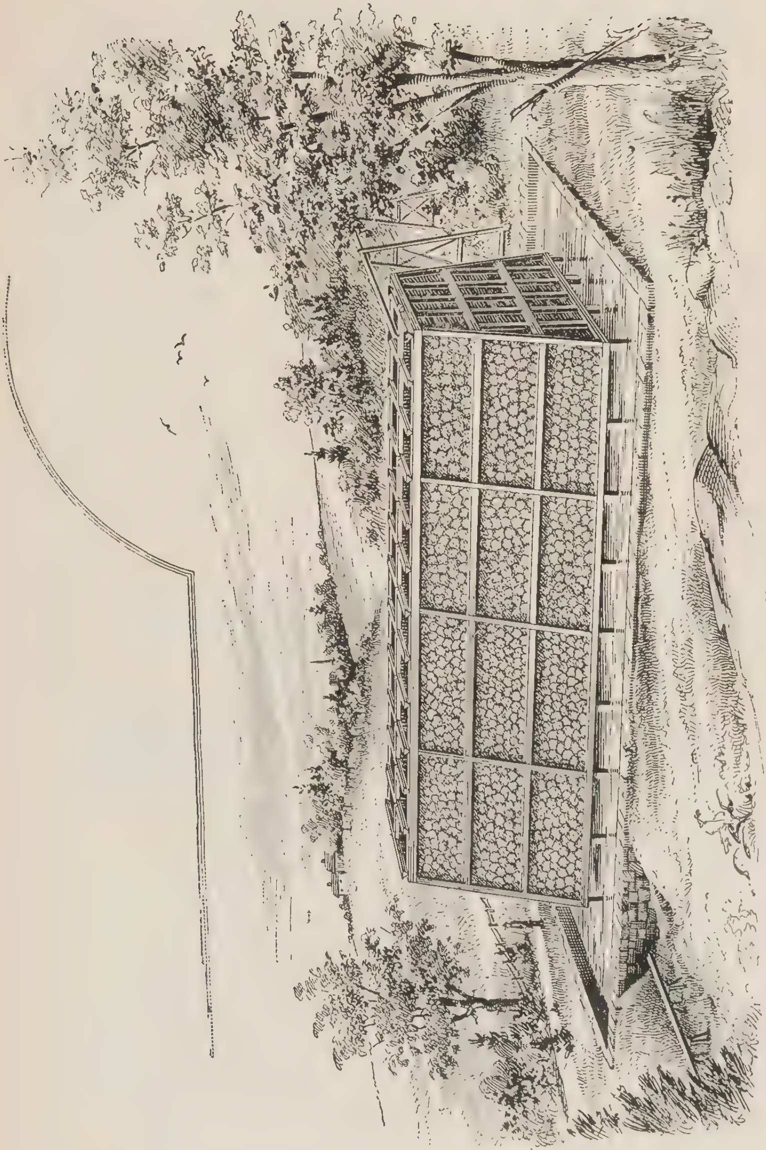


Fig. 1

Sodium peroxide, Na_2O_2, is produced on a commercial scale by heating sodium to 300° C. in a current of dry air. It is a yellowish substance, turning white on exposure to air, and acts as a powerful oxidizing agent. Water decomposes it, forming sodium hydroxide and liberating oxygen. Large quantities are used in bleaching silk and wool.

Sodium hydroxide, $NaOH$, generally known as caustic soda, is extensively employed in the laboratory and in the industries. It is prepared in the pure state by the action of the metal on water; commercially, it is obtained by the action of calcium hydroxide—milk of lime—on sodium carbonate. (See Potassium Hydroxide.)

Sodium hydroxide is deliquescent, freely soluble in water, and absorbs carbon dioxide from the air. For laboratory use

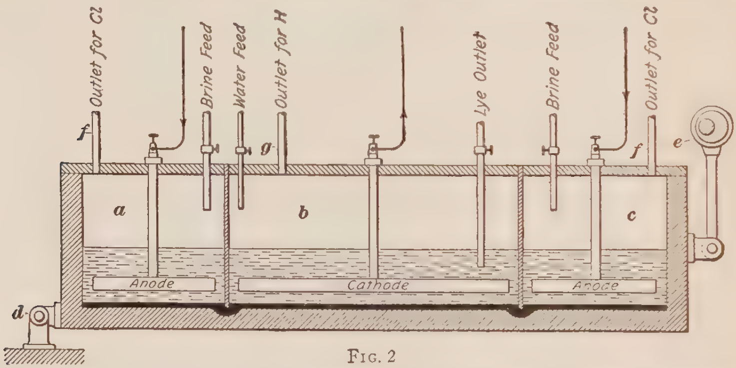


Fig. 2

it usually comes to the market in the form of small sticks, while for commercial purposes it is either sold in solutions of given strengths or the fused product is run into large drums or steel containers.

36. The Castner-Kellner Process.—Many methods have been suggested for the commercial production of chlorine and sodium hydroxide by the electrolysis of a solution of common salt. One of the oldest and most generally used is the Castner-Kellner process, which is worked in this country on a large scale.

Fig. 2 is a diagram that shows the general arrangement but not the relative sizes of the different parts of the apparatus.

The box is constructed of a non-conducting material such as slate, and is about 4 feet long, 4 feet wide, and 6 inches deep. It is divided into the compartments *a, b,* and *c* by means of partitions that extend to within $\frac{1}{16}$ inch from the bottom. As the bottom is covered with a layer of mercury about $\frac{1}{8}$ inch thick, it follows that each compartment is separated from the adjoining one.

A nearly saturated solution of $NaCl$, or brine, is supplied to each of the compartments *a* and *c*, the compartment *b* containing pure water. Carbon anodes are employed and a cathode consisting of an iron grid. The box is pivoted at *d*, the other end being supported by an eccentric rod connecting with an eccentric *e* which makes one revolution per minute and raises and lowers that end through a height of $\frac{1}{2}$ inch. This rocking motion causes the mercury to flow backward and forward between the compartments.

37. As the current passes from the anodes into the solution contained in the compartments *a* and *c*, chlorine is liberated at the anode and removed by suction through the pipes *f, f*. Those portions of the mercury layer that extend into the cells *a* and *c* must be considered as intermediate cathodes. Hence, sodium is liberated at the mercury surface in these cells, the sodium forming an alloy with the mercury. The rocking of the box causes the sodium-mercury alloy to pass into the compartment *b* where the sodium at once combines with water and forms caustic soda and hydrogen, the latter escaping through the pipe *g*. Suitable arrangements are made for a constant supply of a concentrated salt solution to cells *a* and *c* and a withdrawal of the lye solution from the cell *b*. This solution is evaporated and sold in one of the commercial forms of sodium hydroxide, or the solution of sodium hydroxide is converted into sodium carbonate, Na_2CO_3. The apparatus decomposes nearly 130 pounds of sodium chloride during a period of 24 hours, giving about 80 pounds of chlorine and 88 pounds of sodium hydroxide.

38. Sodium Carbonate.—Sodium carbonate, Na_2CO_3, one of the most widely used salts, generally known as soda, or

soda ash, is obtained on a very large scale by a number of methods. One of the oldest methods is that of Le Blanc.

39. In the Le Blanc process salt and sulphuric acid are heated together when the change shown in the following equation takes place:

$$2NaCl+H_2SO_4=Na_2SO_4+2HCl$$

The sodium sulphate, or salt cake, thus obtained is mixed with coal and limestone and again heated, when the sodium sulphate is converted into the carbonate in two steps represented by the equations:

$$Na_2SO_4+2C=Na_2S+2CO_2$$

and $$Na_2S+CaCO_3=Na_2CO_3+CaS$$

The mixture of sodium carbonate and calcium sulphide, known as black ash, is leached with water, dissolving the solu-

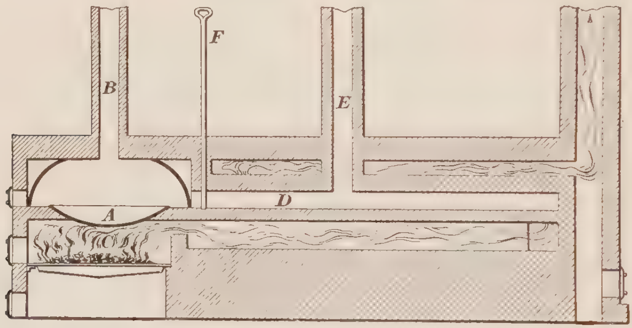


FIG. 3

ble sodium carbonate from the insoluble calcium sulphide. The solution is then evaporated, when the sodium carbonate crystallizes.

40. In the actual operation of the process, the salt and sulphuric acid are charged into the pan *A*, Fig. 3, and are heated by the fire on the grate, the door *F* remaining closed. Large quantities of hydrochloric acid gas are evolved and pass through the flue *B* to a brick tower, where they are condensed. The door *F* is now raised and the partly decomposed salt is transferred to the muffle part *D* of the furnace, where the

decomposition is completed. The hydrochloric acid gas evolved here passes to the condensing towers through the flue *E*.

For about each ton of soda ash produced there is about 1½ tons of waste. This is recovered by pumping the excess carbon dioxide evolved in the burning of the coal and limestone into tall closed cylinders which contain the waste mixed to a creamy consistency with water. The carbon dioxide first forms calcium hydrosulphide and calcium carbonate. The calcium hydrosulphide is then converted into the carbonate with an evolution of hydrogen sulphide. These two steps are represented by the equations:

$$2CaS+H_2O+CO_2=Ca(SH)_2+CaCO_3$$
$$Ca(SH)_2+CO_2+H_2O=CaCO_3+2H_2S$$

The hydrogen sulphide is then burned and produces sulphur and water.

41. The Solvay process, or the ammonia-soda process, has to a large extent superseded the Le Blanc process. This process depends on the double decomposition that occurs when carbon dioxide is passed into a solution of sodium chloride containing ammonia. This process yields a purer product than the Le Blanc process, is less expensive, and gives rise to no noxious by-products.

Brine obtained either directly from the wells or by dissolving rock salt, is purified by treatment with calcium hydroxide, which removes the magnesium salt. The calcium salts are then removed by either sodium carbonate or weak solutions of ammonium carbonate, after which the brine is saturated with ammonia. The ammoniacal brine is then pumped to the carbonating tower. This tower consists of a steel cylinder about 50 feet high and 6 feet in diameter. On the interior, regularly spaced, are placed steel plates with an opening in the center and over these plates are placed dome-shaped diaphragms which are perforated. The ammoniacal brine comes into the tower near the middle under pressure. The carbon dioxide is introduced near the bottom of the tower under a pressure also, of about 25 pounds. It bubbles through the perforated dia-

phragms and comes into intimate contact with the brine. The reaction that takes place is represented by the equation:

$$NH_3+CO_2+NaCl+H_2O=NaHCO_3+NH_4Cl$$

The sodium bicarbonate formed is insoluble in ammonium chloride solution and is precipitated. It is drawn off in the form of a paste, filtered, washed, dried and calcined, thus driving off the ammonium salts and converting the bicarbonate into the neutral carbonate; thus:

$$2NaHCO_3=Na_2CO_3+CO_2+H_2O$$

The carbon dioxide driven off is again utilized by being absorbed by fresh brine. The soda ash produced by this process is white and of unusual purity, containing only traces of salt and sodium bicarbonate. A considerable quantity of sodium carbonate is also produced from cryolite, of which large deposits exist in Greenland. This mineral is calcined with limestone, calcium fluoride and sodium aluminate being formed, according to the equation:

$$\underset{\text{cryolite}}{Na_3AlF_6} + \underset{\substack{\text{calcium}\\\text{carbonate}}}{3CaCO_3} = \underset{\substack{\text{calcium}\\\text{fluoride}}}{3CaF_2} + \underset{\substack{\text{sodium}\\\text{aluminate}}}{Na_3AlO_3} + \underset{\substack{\text{carbon}\\\text{dioxide}}}{3CO_2}$$

The sodium aluminate is dissolved in water and then decomposed by means of carbon dioxide, aluminum hydroxide being precipitated and sodium carbonate remaining in solution. It is then recovered by crystallization.

42. Sodium carbonate crystallizes at ordinary temperatures with 10 molecules of water of crystallization, $Na_2CO_3{\cdot}10H_2O$, in large monoclinic prisms that effloresce in the air and crumble to a white powder. It has an alkaline taste and melts at 849° C. It is soluble in water, the solution having a strong alkaline reaction. The solubility of sodium carbonate is well illustrated by the subjoined data:

100 parts of water at 0° C. dissolve 7.08 parts of sodium carbonate.
100 parts of water at 10° C. dissolve 12.06 parts of sodium carbonate.
100 parts of water at 20° C. dissolve 21.71 parts of sodium carbonate.
100 parts of water at 25° C. dissolve 28.50 parts of sodium carbonate.
100 parts of water at 30° C. dissolve 37.24 parts of sodium carbonate.
100 parts of water at 105° C. dissolve 45.47 parts of sodium carbonate.

The saturated solution boils at 104.6° C. Sodium carbonate is insoluble in alcohol.

43. Acid sodium carbonate, sodium bicarbonate, or bicarbonate of soda, $NaHCO_3$, is prepared by the action of carbon dioxide on the normal carbonate. It forms small monoclinic tabular crystals or a white crystalline powder. It is less soluble in water than the normal carbonate and the solution is much less alkaline. When boiled its solution evolves carbon dioxide. When gently heated the salt itself readily decomposes into sodium carbonate, carbon dioxide, and water.

44. Sodium sulphate, Na_2SO_4, or salt cake, is obtained abundantly commercially as a residue in various chemical processes as, for instance, in the preparation of hydrochloric acid. It is also largely produced as an intermediate product in the manufacture of sodium carbonate by the Le Blanc process. It occurs in nature, anhydrous as thenardite, and hydrated as mirabilite. It crystallizes from solution in large, colorless prisms that have the composition $Na_2SO_4 \cdot 10H_2O$ and are efflorescent in dry air, losing all their water. This is Glauber's salt. The anhydrous salt is soluble in $2\frac{1}{2}$ parts of water at 100° C.

45. Acid sodium sulphate, $NaHSO_4$, or niter cake, is obtained by adding sulphuric acid to the normal sulphate. On cooling the saturated solution oblique rhombic prisms are obtained, which contain 2 molecules of water of crystallization, $NaHSO_4 \cdot 2H_2O$. These crystals are readily soluble in water, and have an acid taste. Alcohol decomposes them into sulphuric acid and normal sulphate, the latter being precipitated.

Acid sodium sulphate, or sodium bisulphate, is also formed when sulphuric acid is brought into contact with such compounds as sodium hydroxide, sodium carbonate, sodium nitrate, etc., at temperatures below 100° C. At higher temperatures the normal sulphate is formed.

46. Sodium Sulphide and Hydrosulphide.—Sodium sulphide, Na_2S, may be obtained by reducing sodium sulphate.

This may be accomplished by heating a mixture of sodium sulphate and carbon, or by heating the sulphate in a current of hydrogen.

Sodium hydrosulphide is prepared by the action of hydrogen sulphide on a solution of sodium hydroxide according to the equation:

$$\underset{\substack{\text{sodium}\\\text{hydroxide}}}{NaOH} + \underset{\substack{\text{hydrogen}\\\text{sulphide}}}{H_2S} = \underset{\substack{\text{sodium}\\\text{hydrosulphide}}}{NaSH} + \underset{\text{water}}{H_2O}$$

47. Sodium Borate.—**Sodium tetraborate,** $Na_2B_4O_7$, better known as borax, occurs as a deposit from evaporation of the waters of certain lakes in Thibet and in the United States.

When a concentrated boiling solution of borax is allowed to cool to 60° C., it deposits octahedral crystals containing 5 molecules of water, while below 60° C. it crystallizes in monoclinic prisms containing 10 molecules of water. This latter is the familiar commercial form. It is somewhat soluble in water, its solution is faintly alkaline, and the crystals effloresce in the air and become opaque.

Borax glass is obtained by fusing the crystalline borax, which swells to a white spongy mass of many times its original volume; this mass afterwards fuses to a clear, glassy mass. It dissolves many metallic oxides very easily and these impart their own peculiar color to the glass. It finds wide employment in blowpipe analysis and in metallurgy. It is antiseptic and is sometimes used as a preservative.

48. Sodium Nitrate.—Sodium nitrate, $NaNO_3$, or Chile saltpeter, is found in large quantities in Peru and Chile. It crystallizes in large rhombohedra very similar to cubes; hence, it is frequently called cubic niter, to distinguish it from the prismatic potassium niter. It is used as a fertilizer and for the manufacture of nitric acid and potassium nitrate.

AMMONIUM

Formula NH_4. Molecular weight 18.04

49. History.—The salts that ammonium forms by direct union show a great similarity to those formed by the metals potassium and sodium. When an ammonium salt such as NH_4Cl is subjected to the action of an electric current the NH_4 ion breaks up into NH_3 and H and the substance NH_4 is not obtained. If mercury is used as the negative electrode, however, the NH_4 ion combines with it to form an amalgam. During its formation the amalgam swells up, becomes frothy, and discharges NH_3 and H. Again, when mercury containing 1 per cent. of sodium is placed in a saturated solution of ammonium chloride, it increases considerably in bulk, becoming a pasty mass, which is the so-called ammonium amalgam. The action in this case is simply the displacement of the sodium ion by the ammonium ion.

These experimental results indicate that an amalgam of mercury and the NH_4 ion temporarily exists and that the NH_4 ion displaces the sodium ion from sodium amalgam. The metals, only, form amalgams with mercury; therefore, it would seem logical to predict that if the ion NH_4 could be isolated it would have the properties of a metal.

50. Ammonium Nitrate.—Ammonium nitrate, NH_4NO_3, is prepared by neutralizing nitric acid with ammonia. It crystallizes in large, transparent prisms which melt at 158° C. It is very soluble in water, alcohol, and liquid ammonia, and produces a notable lowering of temperature in the act of solution. If heated gently, it decomposes into nitrous oxide and water. It is used largely for the manufacture of nitrous oxide, sometimes called laughing gas, for the preparation of freezing mixtures, and for explosives.

51. Ammonium Nitrite.—Ammonium nitrite, NH_4NO_2, is formed by the action of nitrous acid on ammonium hydroxide. When the solution is heated the salt decomposes into nitrogen and water. In order to obtain the crystals,

therefore, the solution must be evaporated under diminished pressure at a temperature under 40° C. Crystals of ammonium nitrite are colorless and deliquescent.

52. Ammonium Carbonate.—Ammonium carbonate, $(NH_4)_2CO_3$, is obtained when ammonia gas is passed through a solution of commercial ammonium bicarbonate, NH_4HCO_3. Exposed to the air, it gives off ammonia and again becomes the bicarbonate. It is also prepared by distilling a mixture of calcium carbonate and ammonium sulphate in an iron retort connected with a leaden receiver. The product is then resublimed in iron vessels. It consists of a mixture of the bicarbonate and ammonium carbamate, NH_4OCONH_2. This is treated with strong alcohol, the carbamate dissolving and the bicarbonate being left.

53. Ammonium Chloride.—Ammonium chloride, NH_4Cl, was formerly obtained from Egypt where it was made by subliming the soot produced by the combustion of camel's dung. It is now produced on a large scale from gas liquor or from the water condensed in the manufacture of illuminating gas from coal. This liquor is heated with lime, ammonia is disengaged and conducted into hydrochloric acid. Ammonium chloride is obtained by simply evaporating the solution. It is then purified by sublimation in stoneware pots which are heated in a furnace, out of which the upper parts of the pots project. The volatilized chloride condenses and the sublimed product is known in trade as sal ammoniac or muriate of ammonia.

It generally occurs as a white or grayish compact mass having a crystalline fibrous structure, which is often striped with brown, owing to the presence of a little iron. It has a sharp and salty taste and dissolves in $2\frac{1}{2}$ parts of cold water and in its own weight of boiling water. It is deposited from a saturated solution in small octahedral crystals grouped together in needles, which present a fern-leaf appearance. At a high temperature it volatilizes without melting.

54. Ammonium Sulphide.—Ammonium sulphide, $(NH_4)_2S$, in the form of a white crystalline mass is obtained

by passing hydrogen sulphide gas with ammonia gas into a vessel cooled by a mixture of salt and ice. It is readily soluble in water and is rather unstable, decomposing at ordinary temperature into free ammonia and ammonium hydrosulphide, NH_4HS.

When strong ammonium hydroxide is saturated with hydrogen sulphide at a low temperature, a colorless solution of NH_4HS results. In contact with the air this soon becomes yellow from the formation of ammonium polysulphides, $(NH_4)_2S_x$. The letter x in this formula indicates an unknown number of sulphur atoms. A solution of yellow ammonium sulphide, $(NH_4)_2S_x$, may be readily obtained by dissolving a small quantity of sulphur in a saturated solution of ammonium sulphide, $(NH_4)_2S$.

55. Ammonium Bromide and Ammonium Iodide. Ammonium bromide, NH_4Br, and ammonium iodide, NH_4I, are largely employed in photography. The former crystallizes in white cubes having a pungent, salty taste; it is volatile at a high temperature without decomposition and is soluble in water and alcohol. The latter crystallizes in colorless cubes, which gradually become yellow and even brown from the separation of iodine. It is hydroscopic and odorless, has a sharp, saline taste, and is extremely soluble in water and alcohol. It is volatile at a high temperature with decomposition without melting.

56. Ammonium Phosphate.—The most important of the compounds of ammonium and phosphorus is the secondary ammonium sodium phosphate, or microcosmic salt, $NH_4NaHPO_4 \cdot 4H_2O$. It is prepared by mixing hot strong solutions of ammonium chloride and sodium phosphate, thus:

$$Na_2HPO_4 + NH_4Cl = NH_4NaHPO_4 + NaCl$$

It forms large transparent, monoclinic crystals that are very soluble. When heated it boils violently, giving up water and ammonia, finally forming a transparent glass of sodium metaphosphate which is used in blowpipe work for the detection of various metals.

LITHIUM

Symbol Li. Atomic weight 6.94

57. History and Occurrence.—Lithium oxide was recognized first as a new substance by Arfvedson, a Swedish chemist, in 1817. The metal was first prepared pure by Bunsen and Matthiessen in 1855. Lithium is a comparatively rare metal, being found principally in the rare minerals amblygonite, spodumene, petalite, lepidolite, and triphylite; the water of many mineral springs contains it in considerable quantity, while traces of it have been detected by means of the spectroscope in sea-water, in many minerals and meteorites, as well as in various plants.

58. Preparation and Properties.—Metallic lithium is best obtained by the electrolysis of lithium chloride. On a large scale a mixture of potassium and lithium chlorides is electrolyzed. It is a brilliant, silver-white metal, somewhat softer than lead, and it tarnishes in the air. It is remarkable as the lightest of the solid metals, having a specific gravity of only .534 at 20° C. It melts at 186° C., is ductile, and can be welded at ordinary temperatures, and burns in the air when more strongly heated. It bears a general resemblance to potassium and sodium, but it is harder and less easily oxidized than these metals. It decomposes water rapidly at ordinary temperatures, but not so energetically as to cause the hydrogen evolved to ignite. Its spectrum is characterized by an intense crimson line.

COMPOUNDS OF LITHIUM

59. Some of the principal compounds of lithium are lithium chloride, $LiCl$, a deliquescent, fusible, and volatile salt; the oxide, Li_2O, and the hydroxide, $LiOH$, the latter a caustic, strongly alkaline substance; the carbonate, Li_2CO_3; the sulphate, Li_2SO_4; and the phosphate, Li_3PO_4, all of which are well-defined salts.

RUBIDIUM

Symbol Rb. Atomic weight 85.45

60. Preparation and Properties.—Rubidium was first detected by Bunsen in 1860 by means of the spectroscope. Its spectrum contains two characteristic dark-red lines, whence its name, which is derived from the Latin word *rubidus,* meaning dark-red. It has since been found in small quantities in various mineral waters, and in the mineral lepidolite, as well as in the ashes of various plants. By distilling the carbonate with charcoal, rubidium is obtained as a soft, white metal with a tinge of yellow and a specific gravity of 1.52. It melts at 38.5° C. and volatilizes below a red heat. It is more easily oxidized than potassium to which it is closely related. It burns on water with a flame of almost the same color as potassium. It is best preserved in hydrogen and, next to cæsium, is the most electropositive of all the metals. It dissolves in cold water, in acids, and in alcohol with great energy, giving out hydrogen.

COMPOUNDS OF RUBIDIUM

61. The salts of rubidium resemble closely those formed by potassium. The chloride crystallizes in cubes, dissolves in its own weight of water at 150° C., and forms a double salt with platinum chloride. The nitrate, $RbNO_3$, resembles saltpeter in its properties, but crystallizes in hexagonal prisms. The carbonate, Rb_2CO_3, is an alkaline deliquescent salt very soluble in water. The sulphate, Rb_2SO_4, is isomorphous with potassium sulphate.

CÆSIUM

Symbol Cs. Atomic weight 132.81

62. Cæsium was discovered simultaneously with rubidium and in the same mineral water. Its name is derived from the Latin word *cæsius,* meaning sky blue, and has reference to the two bright blue lines in its spectrum. It is widely dis-

tributed in small quantities in the rare mineral pollux as cæsium aluminum silicate, in many mineral springs, and in the ash of certain plants, as tobacco, tea, etc. Its specific gravity is 1.88. Cæsium is very similar to the other alkali metals, is a silver white, very soft, ductile metal, melting at 28.45° C. Heated in the air, it burns rapidly, and takes fire when thrown on water. It is kept under petroleum and is the most electropositive metal known. It is prepared by igniting the hydroxide with aluminum in a nickel crucible.

GENERAL REVIEW OF THE GROUP OF ALKALI METALS

63. Cæsium, rubidium, potassium, sodium, and lithium constitute a group of elements conspicuous for their highly electropositive character, the powerfully alkaline nature of their hydroxides, and the general solubility of their salts. Their chemical characters and functions are directly opposite to those of the electronegative group embracing fluorine, chlorine, bromine, and iodine; like those elements, they exhibit a gradation of properties. Thus, cæsium appears to be the most highly electropositive member, rubidium the next, then potassium and sodium, while lithium is the least electropositive; and, just as iodine, the least electronegative of the halogen group, possesses the highest atomic weight, so cæsium, the least electronegative (or most electropositive) of the alkali metals, has a higher atomic weight than any other member of its group. As in the case of the halogens, these are all monovalent elements.

Attention has been called to the gradation of properties of the elements. In some of their salts a similar gradational relation may be observed; the carbonates, for instance, of cæsium, rubidium, and potassium are highly deliquescent, absorbing water greedily from the air, while carbonate of sodium is not deliquescent, and carbonate of lithium is only sparingly soluble in water.

COPPER GROUP

GENERAL REMARKS

64. The relationship existing between the metals of the copper group, namely, copper, silver, and gold, is not nearly as close as the relationship between the members of the alkali group. The members of the copper group are not nearly so active chemically as those of the alkali group, but they form a greater variety of compounds. The members of the alkali group are monovalent in all their salts, but all the members of the copper group form some compounds in which their valence is greater than 1. Copper forms one series of salts in which it is monovalent and one in which it is bivalent. Gold forms one series in which it is monovalent and one in which it is trivalent. Silver is nearly always monovalent, but forms a few compounds in which its valence appears to be greater than 1. The chemical activity of the members of this group —copper, silver, and gold—decreases as the atomic weight increases.

COPPER

Symbol Cu. Atomic weight 63.57

65. History and Occurrence.—Copper has been known from the earliest times. The Romans obtained it from the island of Cyprus and called it *aes Cyprium,* a term that afterwards became *cuprum,* from which the English word copper is derived. It is found abundantly in nature both free and in combination. Native copper occurs in masses of great size near Lake Superior, while sulphide and carbonate ores are found in Canada, Montana, and Arizona. Large deposits of copper-bearing ore are also found in Australia, Chile, Peru, and in Russia and Siberia. The names of the principal copper

ores and their chemical compositions are as follows: Cuprite, Cu_2O; cuprous sulphide, CuS, in copper glance, and associated with sulphide of iron in copper pyrites; as basic carbonate, in malachite, $Cu_2(OH)_2CO_3$; and in azurite, $Cu_3(OH)_2(CO_3)_2$.

66. Preparation.—The methods used for the extraction of copper vary with the ore under treatment. The oxides and carbonates are simply heated with charcoal or other fuel with the addition of some silicious flux. The process of extracting copper from a mixture of copper sulphides and oxidized ore is a more complex operation.

67. Chemical Reactions.—Copper possesses a greater affinity for sulphur and a smaller affinity for oxygen than the metals (especially iron) with which it is associated.

The extraction of copper from sulphide ores is not easy and requires careful and prolonged treatment. The various processes through which the copper ore must pass before a sufficiently pure copper is obtained, may be classified as follows: (*a*) Heating and roasting; (*b*) calcination; and (*c*) poling.

68. Method of Extraction From Copper Ore.—During the heating and roasting process the ore is first moderately heated; part of the sulphur and arsenic is oxidized and passes off as sulphur dioxide and arsenic trioxide, respectively. This operation is regulated so that the sulphur retained is sufficient to combine with the whole of the copper to form cuprous sulphide, Cu_2S, the iron and part of the copper being transformed into oxide. The charge is then brought to a fusion at a higher temperature when the ferrous oxide enters into combination with the silica, either originally contained in the ore or added to the charge to form a slag of ferrous silicate. The iron is removed by repetition of roastings and fusions.

69. In the calcination process the cuprous sulphide is first partly oxidized during a moderate temperature. Then the temperature is raised so that the cuprous oxide formed may react with the sulphide:

$$2Cu_2O+Cu_2S=6Cu+SO_2$$

The remainder of the sulphur is thus eliminated and metallic copper obtained. Any sulphide of iron that still remains is also acted on by the cuprous oxide as follows:

$$3Cu_2O+FeS=6Cu+FeO+SO_2$$

70. In the heating, roasting, or calcination of ores and materials used or manufactured by chemical plants, the reverberatory furnace is frequently used, and a brief description of this type of furnace is therefore important.

The material to be heated is placed on the bed or hearth *B* of the furnace, Fig. 4, and exposed to the direct action of the flame and gases which pass from one end *F* of the furnace to the other and are deflected toward the hearth by the semi-

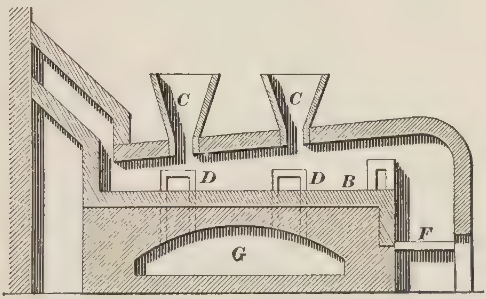


FIG. 4

arched construction of the furnace roof. The charge is introduced at the hoppers *C* and spread over the bed of the furnace, being worked from the doors *D* and finally withdrawn through openings in the bed of the furnace which are not shown in the figure, and shot down into the vault *G*, while the volatile products escape through the flue. The course of the discharge exits is shown by dotted lines in the illustration.

71. In the poling process, the crude, or blister, copper obtained by any one of the numerous processes in use is further refined by an operation known as poling. In this operation, the crude copper is melted in an oxidizing atmosphere on the hearth of a furnace. Coal is then sprinkled on the surface of the molten metal and the mass agitated with a

log of green wood. In this manner any cuprous oxide is reduced by the action of the carbon in the coal and by the hydrocarbons* of the wood passing through the molten metal.

72. Other Processes.—Copper, 99.8 per cent. pure, is now obtained in this country by electrolytic processes in which a current of electricity is passed through a bath of copper sulphate in which are suspended crude copper ingots or plates which act as anodes and pure sheets of copper which act as the cathodes. When the current is turned on copper is dissolved from the anodes and is deposited on the cathodes, while the impurities are either dissolved or sink about the anodes to the bottom of the bath.

73. The copper in low-grade sulphide ores is now most profitably recovered by what is called the flotation process. The separation of copper in this process is dependent upon the fact that when the ore is finely ground and violently agitated in water containing an oil, preferably pine oil, by means of compressed air, a tough froth is formed which floats the metallic particles of copper but which allows the gangue, or ordinary rock, to sink to the bottom of the tank.

74. Properties.—Copper is a lustrous, sonorous metal of a peculiar red color and which, in thin sheets, transmits a greenish-blue light. Its specific gravity is 8.95 and it is somewhat softer than iron. When rubbed with the hand it exhales a peculiar disagreeable odor. It conducts heat and electricity very readily. It may be drawn into fine wire or beaten into thin leaves, as its tenacity is considerable, being second only to iron in this respect. Copper melts at 1,065° C. in air and may be volatilized by the heat of the oxyhydrogen blowpipe. It is unaltered in dry air at ordinary temperatures, but it absorbs oxygen in the presence of moisture and carbon dioxide. Green spots then appear on the surface, constituting a basic carbonate of copper, $CuCO_3 \cdot Cu(OH)_2$, which is the compound commonly, but erroneously, known as verdigris. At a high temperature it readily absorbs oxygen, being converted

*Hydrocarbons. (See *Organic Chemistry*.)

into red cuprous oxide if the metal is in excess. The oxidation of copper is accelerated if the metal is in a state of fine

TABLE I

ALLOYS OF COPPER

Name of Alloy	Approximate Percentage Composition								
	Cu	Zn	Sn	Ni	Pb	Fe	Sb	P	Ag
Albata metal	62	32		8					
Babbitt metal	2		91				7		
Bath metal	55	45							
Brass, Common yellow	66	34							
Brass, for rolling	73	23	4						
Brass, Common castings	84	5	11						
Brass, Hard castings	75	7	18						
Brass, Propeller	84	5	11						
Bronze	85	5	10						
Bronze, Cannon	90		10						
Bronze, Coinage	95	1	4						
Phosphor-bronze	90		9					1	
Bell metal, Large	75		25						
Bell metal, Small	80		20						
Chinese silver	58	17		12		11			2
Chinese gongs	81		19						
German silver	9	28		35		28			
Gun metal	89		11						
Mosaic gold	66	34							
Pinchbeck	83	17							
Retz alloy	74		12		9		8		
Statuary	91	6	2		1				
Speculum metal	66		34						
Telescope mirrors	67		33						
White metal, Hard	70	26	4						

division; in fact, when very finely powdered it often takes fire spontaneously. Weak acids, alkalies, and saline solutions act

on it slowly in the presence of air, sulphuric and hydrochloric acids have little or no action on copper in the cold, and the action of hydrochloric acid, even when hot, is very slow. On the other hand, hot sulphuric acid attacks copper rapidly. Nitric acid attacks copper rapidly, no matter what the temperature or concentration of the acid.

75. Uses of Copper.—With the possible exception of iron, copper is probably the most useful metal. It is much employed for the construction of boilers, stills, etc. Owing to its high electric conductivity, enormous quantities of it are used in electrical construction for cables, dynamos, etc. Sheet copper is used as a sheathing for the bottoms of ships, for roofing, etc. Large quantities of copper are also used in making coins of small denominations and in alloys.

76. Pure copper although very ductile does not make good castings, as it does not fill out the molds owing to its unequal contraction on cooling. Numerous alloys, however, such as the brasses and bronzes, in which copper is the principal ingredient, are extensively used for making castings, and are shown in Table I.

COMPOUNDS OF COPPER

77. Copper forms two series of salts. It acts as a divalent element in the principal series which contains such compounds as $CuCl_2$, $CuSO_4$, CuS, and CuO; these are generally spoken of as copper compounds, though to distinguish them from the other series they are frequently called cupric compounds. Another series of salts, of which some of the members are apparently represented by the formulas $CuCl$, Cu_2O, Cu_2S, etc., is also known; these are called cuprous compounds. In this series, copper appears to be monovalent, though it has been suggested that in these compounds copper is also divalent, and that the formulas should be written Cu_2Cl_2, etc., or $\begin{array}{l} Cu—Cl \\ | \\ Cu—Cl \end{array}$, etc. A determination of the vapor density of cuprous

chloride seemed to point to the double formula, Cu_2Cl_2, but the results were not conclusive, and so long as nothing definite is known of the composition of these compounds, it seems reasonable to use the simplest formula.

78. Cuprous Oxide.—Cuprous oxide, Cu_2O, is found in nature as cuprite, in either vitreous masses or red octahedral crystals. It is ordinarily prepared in the wet way by boiling a solution of copper acetate with glucose (corn or grape sugar); a bright-red, crystalline powder is precipitated which is anhydrous cuprous oxide. When heated in contact with air it absorbs oxygen and is converted into cupric oxide.

When potassium hydroxide is added to a solution of cuprous chloride, a yellow precipitate of cuprous hydroxide is thrown down. Cuprous oxide is used to impart a red color to glass.

79. Cupric Oxide.—Cupric oxide, CuO, occurs in nature as the mineral melaconite. It may be prepared by heating the metal in the air or by calcining the hydroxide, carbonate, or nitrate. It occurs in isometric forms—perhaps also in orthorhombic—but is generally massive. Its specific gravity is 6.3 and it fuses without change at a bright-red heat. Cupric oxide is easily reduced by both hydrogen and charcoal with formation of either water or carbon dioxide, and hence is frequently used in organic analysis. It colors glass a beautiful emerald green. Cupric hydroxide, $Cu(OH)_2$, is precipitated as a pale-blue substance on adding sodium hydroxide to a cold solution of a cupric salt. It is strongly basic and forms numerous salts.

80. Cupric Sulphide and Cuprous Sulphide.—Cupric sulphide, CuS, is found in nature as the mineral covellite. It is hexagonal in its crystallization, is of bluish-black color, with a semimetallic luster, and has a specific gravity of 4.6. It is the black precipitate obtained when copper salts are precipitated by hydrogen sulphide. Cuprous sulphide, Cu_2S, also occurs in nature, forming the mineral chalcocite. It may be prepared by exposing finely divided copper or copper foil to sulphur vapor. It crystallizes in orthorhombic prisms, is blackish gray in color, has a metallic luster which is frequently tinged with green, and is easily fusible.

81. Cupric Sulphate.—Cupric sulphate, $CuSO_4$, more commonly known as copper sulphate or blue vitriol, can be prepared by treating almost any cupric compound as the hydroxide, carbonate, etc., with sulphuric acid. It is frequently prepared on a large scale by treating cupric sulphide with sulphuric acid. The simplest process consists in heating copper turnings and clippings with sulphuric acid, sulphur dioxide being disengaged and cupric sulphate formed. On a commercial scale, the operation is conducted in lead-lined wooden tanks heated by steam.

Cupric sulphate crystallizes in large, blue, prismatic crystals that contain 5 molecules of water. When exposed to dry air, they effloresce superficially; heated to 100° they lose 4 molecules of water, disengaging the fifth only at 220° C. to 260° C. The anhydrous salt is white. At a high heat cupric sulphate is decomposed into cupric oxide, sulphur dioxide, and oxygen. Cupric sulphate dissolves in 4 parts of cold and 2 parts of boiling water and the concentrated solution has a pure blue color. It is insoluble in alcohol.

When an excess of ammonia is added to a solution of cupric sulphate a beautiful, dark-blue liquid is obtained. It contains ammoniacal cupric sulphate, $CuSO_4 \cdot 4NH_3 \cdot H_2O$, which separates as dark-blue crystals when alcohol is added to the aqueous solution.

There are several basic sulphates of copper representing compounds of cupric sulphate and cupric hydroxide. One of them is obtained as a green powder when a solution of cupric sulphate is digested with cupric hydroxide. The bluish precipitates obtained by the incomplete precipitation of solutions of cupric sulphate with potassium hydroxide are basic sulphates.

Cupric sulphate is employed as a caustic applicable to diseases of the eye. In the arts, it is used in the preparation of blue ashes, a mixture of calcium sulphate and cupric hydroxide, made by decomposing cupric sulphate with milk of lime. It is much used in dyeing, particularly in dyeing black on wool and cotton; it is also employed for preserving wood. Large quantities of sulphate of copper are employed for electrotyping and electric batteries.

82. Carbonates of Copper.—When cold solutions of sodium carbonate and cupric sulphate are mixed, a bluish-green precipitate is obtained and at the same time carbon dioxide is disengaged. The precipitate becomes green when washed with warm water. It is known as mineral green, and can be regarded as a combination of 1 molecule of cupric carbonate with 1 molecule of cupric hydroxide. Its formula may be written:

$$CuCO_3{\cdot}Cu(OH)_2$$

A similar compound exists in nature, constituting malachite. This mineral occurs in green masses. When cut and polished it presents veins of various tints and is fashioned into ornamental objects.

Azurite, or mountain blue, which crystallizes in beautiful, blue, oblique rhombic prisms, can be regarded as a compound of 2 molecules of cupric carbonate with 1 of the hydroxide. Its formula is $2CuCO_3{\cdot}Cu(OH)_2$.

83. Copper Acetate.—Copper acetate, $Cu(C_2H_3O_2)_2$, may be prepared by dissolving cupric oxide in acetic acid or by the reaction which takes place when solutions of copper sulphate are mixed with a solution of the acetates of other metals such as lead or calcium. Copper acetate is soluble in hot or cold water, from which it crystallizes in dark-green prisms which are soluble in alcohol and ether.

Copper acetate is used in textile manufacture, in paints, in medicine, and as an insecticide.

84. Basic Copper Acetate.—Basic copper acetate, $CuO{\cdot}Cu(C_2H_3O_2)_2{\cdot}6H_2O$, is also commonly called copper subacetate and green verdigris. It is not a true chemical compound as the formula seems to indicate, but consists of a mixture of basic acetates of copper.

Verdigris is usually made by exposing copper sheets to the alternate action of acetic acid and the air over a period of from 6 to 8 weeks. The product thus obtained is used as a pigment, insecticide, and for dyeing and printing fabrics.

HALOGEN COMPOUNDS OF COPPER

85. Copper forms two series of haloid salts, the cuprous CuF, $CuCl$, and the cupric CuF_2, $CuCl_2$, etc. These latter haloid salts, though in general tolerably stable in solution and obtainable therefrom on concentration in crystals, are readily decomposed by heat and converted into the cuprous form in which they are insoluble in water. The cupric iodide, however, breaks up even in the moist condition and the precipitate obtained on adding potassium iodide to solutions of cupric salts consists of white cuprous iodide and iodine. Cuprous salts give under the same circumstances a pure white precipitate of cuprous iodide.

86. Cuprous Chloride.—Cuprous chloride, $CuCl$, is formed by burning copper in chlorine or by the action of reducing agents such as sulphurous acid, zinc dust, or metallic copper, on cupric chloride. If, therefore, cupric oxide is dissolved in concentrated hydrochloric acid, the solution when boiled with excess of copper contains cuprous chloride, which is deposited as a white powder when it is poured into a large quantity of water. This, on exposure to air, turns green, owing to the formation of a basic chloride. The solution of cuprous chloride absorbs carbon monoxide and is used for determining the amount of this gas in certain gaseous mixtures; in presence of acetylene, C_2H_2, a basic cuprous acetylide is formed, from which pure acetylene may be liberated by treatment with acid.

87. Cupric Chloride.—Cupric chloride, $CuCl_2$, is formed when metallic copper or cuprous chloride is heated in excess of chlorine. It crystallizes in green needles with 2 molecules of water. It is obtained as a green solution by digesting cupric oxide with concentrated hydrochloric acid and adding water.

SILVER

Symbol Ág. Atomic weight 107.88

88. History and Occurrence.—Silver has been known in the metallic form from the earliest historic times. The ancient alchemists gave to it the name of Luna, from its bright white color.

It is found in a free state in the United States, Mexico, Peru, and many other countries. Its most important ores are argentite, Ag_2S; pyrargyrite, Ag_2SbS; and horn silver, $AgCl$. It is found also in combination with lead sulphide, copper sulphide, and many other ores.

89. Preparation.—The process employed for the extraction of silver varies, naturally, with the quality of the ore. At Freiberg, in Germany, the ore—an impure sulphide—is roasted with 10 per cent. of salt; the resulting mass is ground to a fine powder, and agitated in revolving barrels containing water and scrap iron, by which the silver is reduced to the metallic state. Mercury is then added to dissolve the silver, and by distilling the amalgam thus obtained, the silver is left pure. In this country most of the silver is obtained in the lead-smelting process or in connection with gold by amalgamation or one of the lixiviation processes.

90. The commonest method employed in the United States consists of mixing the silver ore with other ores rich in lead and smelting this mixture with iron (either as scrap or as iron ore), limestone, and coke in a blast furnace. The silver-lead alloy obtained (base bullion) usually contains gold, some copper, antimony, bismuth, etc. The base bullion is melted and then allowed to cool almost to the point of solidification, when the copper, bismuth, antimony, etc. rise to the top of the molten mass and are skimmed off. The greater portion of the lead in the base bullion is then removed either by melting the mass and allowing it to cool slowly, when pure lead crystallizes out, or by adding zinc to the molten mass and then cooling it. An alloy of lead-silver zinc, rich in silver,

now rises to the surface and is skimmed off. The zinc is expelled by distillation and the lead removed by cupellation. Any gold contained in the base bullion will be found with the silver, after cupellation.

91. Cupellation.—By cupellation is ordinarily meant the volatilization of lead and formation of lead oxide, PbO, in gold and silver refining processes. On a large scale, a cupel is made by depressing the bed of a reverberatory furnace, thus forming a shallow basin. This basin is lined with bone-ash to prevent injury to the furnace and the charge of base bullion is then placed in it. The furnace is then fired

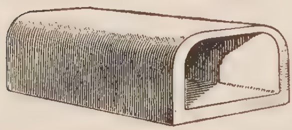


FIG. 5

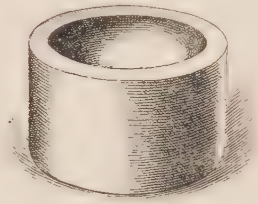


FIG. 6

and a slow current of air passed over the molten metal. The oxygen of the air combines with the lead and forms lead oxide, which is absorbed by the bone-ash lining.

On a laboratory scale, the process of cupellation is carried out by placing the small lead *button* containing gold and silver on a small bone-ash cupel which, in turn, with its charge, is placed on the floor of a small muffle furnace. The muffle shown in Fig. 5 is about one-fifteenth size. The bone-ash cupel used in laboratory work, shown in Fig. 6, is about three-quarter size.

92. Properties.—Pure silver is a remarkably white, lustrous metal of specific gravity 10.5 and capable of taking a high polish. It is the best metallic conductor of heat and electricity known, is harder than gold, and is very ductile and malleable, although working silver hardens it and it must be softened repeatedly by heating to a dull redness. It crystallizes in regular octahedra, melts at 961.5° C., and may be distilled at the highest temperature of the oxyhydrogen blowpipe.

When melted, silver is capable of absorbing twenty-two times its own volume of oxygen, which, however, is again evolved when it solidifies. It is unaltered in the air at any temperature, though it is readily acted on by chlorine, sulphur, and phosphorus. It is readily soluble in nitric acid, but dissolves with difficulty in hydrochloric and sulphuric acids. The alkalies have no action on it; for this reason silver vessels are sometimes used in the laboratory for fusing potassium hydroxide and concentrating its solution. By the action of certain reducing agents on silver salts, the metal is obtained in a finely divided condition in which form it shows brilliant golden, ruby, blue, and other tints.

93. Uses.—Owing to its softness silver is rarely used in the pure state. It is generally alloyed with copper, which, while it greatly increases its hardness, scarcely alters its color.

The silver-coin alloy of the United States and France contains 10 per cent. of copper, that of England 7.5 per cent. The silver used in silver plate usually contains from 70 to 95 per cent. of pure silver.

94. By means of the process of electroplating, the surface of baser metals is provided with a coating of silver, by connecting them to the negative pole of the galvanic battery and immersing them in a solution made by dissolving silver cyanide in potassium cyanide (a solution of potassium cyanide in 10 parts of water with 3.5 grams of silver chloride dissolved in each pint of the liquid, will answer the purpose nicely), the positive pole being connected with a silver plate, also immersed in the solution. The electric current gradually decomposes the silver cyanide and this metal is deposited on the object connected with the negative electrode, while the cyanogen liberated at the silver plate attacks the silver, so that the solution is always maintained at the same strength; the quantity of silver dissolved at this electrode is precisely equal to that deposited at the opposite one.

95. Glass may be silvered by the use of the following solutions:

1. Silver nitrate, 30 grams.
   Distilled water, 300 cubic centimeters.
2. Potassium hydroxide, 30 grams.
   Distilled water, 300 cubic centimeters.
3. Glucose, or grape sugar, 15 grams.
   Distilled water, 300 cubic centimeters.

By the use of these solutions about 200 to 250 square inches of surface may be silvered.

To finish the preparation of the final silvering solution, ammonia is added, drop by drop, to solution 1 until the turbidity first produced is just cleared; then solution 2 is slowly added to solution 1, and just enough ammonia is again added, drop by drop, to clear up the combined solutions. Solution 3 is then added to the mixture of solutions 1 and 2, and after thorough mixing the solution is ready to be applied to the glass.

COMPOUNDS OF SILVER

96. Silver Nitrate.—Silver nitrate, $AgNO_3$, or lunar caustic, is prepared by dissolving pure silver in nitric acid and allowing it to crystallize, or the solution is evaporated and the residue fused and cast into sticks. It crystallizes in rhombic tables or plates that melt at 218° C., that have a specific gravity of 4.3, and are readily soluble in alcohol and water. It is odorless, has a bitter, metallic taste and a caustic action, rapidly blackening and destroying organic matter. It does not blacken in the air unless organic matter is present. Thus, it stains the fingers black when exposed to the light, but the stain may be removed by potassium cyanide or, more safely, by tincture of iodine.

Silver nitrate is used in photography, in medicine, and to some extent in marking inks for linen and cotton goods, since the deposit of metallic silver formed on exposure to the light is not affected by washing.

97. Silver Chloride.—Silver chloride, $AgCl$, occurs in nature as the mineral cerargyrite. It may be obtained by the direct union of silver and chlorine or by precipitating a solu-

tion of silver nitrate by a soluble chloride. A white, curdy mass, soluble in ammonium hydroxide, but insoluble in nitric acid, is thrown down which, on drying, becomes a white powder. When heated to 451° C., it fuses to a dark-yellow liquid, and on cooling it solidifies to a translucent mass resembling horn, whence the name horn silver is sometimes applied to it. It has a specific gravity of 5.5, crystallizes in isometric forms, and turns black on exposure to light. For the latter reason it is used in photography.

If freshly precipitated and moist silver chloride is placed on a sheet of zinc, in a short time a dark color will appear on the borders of the chloride, and the whole of that body will soon be converted into a dark-gray powder of finely divided silver, zinc chloride being formed at the same time. This reaction takes place much more rapidly if the silver chloride is moistened with hydrochloric acid, in which case the reduction is effected by nascent hydrogen produced by the action of the hydrochloric acid on the zinc.

98. Silver Bromide and Silver Iodide.—Silver bromide, *AgBr*, and silver iodide, *AgI*, are both found in nature in Mexico and Chile. Silver bromide may be obtained on adding hydrobromic acid, or a bromide of an alkali metal, to a solution of silver nitrate, as a yellowish-white, curdy precipitate which is insoluble in nitric acid and nearly so in dilute ammonia—whereby it is distinguished from silver chloride—and melts at 426° C., forming a reddish liquid. The precipitated bromide when exposed to light, changes its color and assumes a grayish tint.

Silver iodide is a yellow, insoluble precipitate produced by adding silver nitrate to potassium iodide. It is insoluble, or nearly so, in ammonia, and in this respect forms an exception to silver salts in general. It blackens on exposure to light and melts at about 555° C. to a yellow liquid, which becomes brown on continued heating.

99. Silver Oxide.—Silver oxide, Ag_2O, is usually prepared by adding a strong, hot solution of silver nitrate to one of potassium hydroxide. It is a dark-brown powder with a

specific gravity of 7.5. It is readily decomposed by heat and partly decomposed by light into metallic silver and oxygen. It is only slightly soluble in water when freshly prepared; ammonia dissolves it readily, the solution depositing a violently explosive crystalline compound. Silver hydroxide, $AgOH$, is a strong base, is alkaline, and becomes silver oxide on heating to 60° C.

100. Silver Nitrite.—Silver nitrite, $AgNO_2$, was first obtained by Proust. It is prepared by mixing warm solutions of silver nitrate and potassium nitrite. On cooling, silver nitrite separates in white crystalline needles which are slightly soluble in water, and which decompose without fusion when heated to 180° C. It dissolves in boiling water with partial decomposition.

101. Silver Sulphate.—Silver sulphate, Ag_2SO_4, is the final product obtained when silver sulphide is roasted in the air. It is also prepared by dissolving metallic silver in hot sulphuric acid. It crystallizes in small rhombic prisms that are isomorphous with anhydrous sodium sulphate. It is slightly soluble in water, fuses at 660° C., and decomposes at a high temperature.

102. Silver Sulphite.—Silver sulphite, Ag_2SO_3, is precipitated as a white curdy mass when sulphurous acid is added to a solution of silver nitrate. It is insoluble in water, blackens in the light, and decomposes at 100° C.

103. Silver Orthophosphate.—Silver orthophosphate, Ag_3PO_4, is formed as a yellow precipitate when a solution of sodium orthophosphate is added to a solution of silver nitrate. It is soluble in nitric acid, but insoluble in water. It is affected by the light, turns brown on heating, and melts at 849° C. It is used in photography.

104. Silver Arsenite and Silver Arsenate.—Silver arsenite, Ag_3AsO_3, is obtained as a yellow precipitate insoluble in water and alcohol when a mixture of the solutions of silver nitrate and arsenious acid is made slightly ammoniacal in the cold. If this solution is boiled, metallic silver separates. It

is soluble in an excess of ammonium hydrate. Silver arsenate, Ag_3AsO_4, is obtained as a reddish-brown precipitate when silver nitrate is added to arsenic acid. It is soluble in nitric acid and ammonium hydroxide.

105. Silver Sulphide.—Silver sulphide, Ag_2S, occurs in nature as silver glance, or argentite, crystallized in regular octahedrons. It is soft and can be scratched with the finger nail. It is prepared either by heating together silver and sulphur or by precipitating silver salts with hydrogen sulphide.

106. Silver Fluoride.—Silver fluoride, AgF, is formed when the oxide or carbonate is dissolved in hydrofluoric acid. It is soluble in little more than half its weight of water, the solution having a strongly alkaline reaction. The salt takes up about 840 times its volume of ammonia.

GOLD

Symbol Au. Atomic weight 197.2

107. Occurrence.—Gold occurs widely distributed in nature, though as a rule in small quantity. It is almost always found in the metallic state usually associated, however, with certain quantities of silver, copper, or iron, and also in special ores with bismuth and tellurium. Many minerals such as galena, iron pyrites, and zinc blende, contain traces of gold. Though one of the rare metals, it is widely distributed; the chief localities where it is mined are the Rocky Mountain and Pacific Coast States in this country; Australia and South Africa. It is found generally in quartz veins intersecting metamorphic rocks of various ages, and in the gravel that has resulted from the disintegration of these rocks. In consequence of the value of the metal and because of the simplicity of the methods by which it is worked, a deposit containing as little as 1 part of gold in 500,000 may sometimes be worked profitably.

108. Preparation.—To extract gold from gold-bearing quartz, the whole is first powdered roughly by mechanical

means and then subjected to separation in sluices so arranged that the heavier particles containing the gold collect at the bottom of the sluice, while the gangue is carried off by the stream of water. The gold is separated by causing it to form an amalgam with mercury or to collect on amalgamated copper plates. The mercury is finally distilled off, leaving the gold as residue.

109. In the chlorination process the ore (iron pyrites or sulphide concentrates from stamp mills) is roasted, so that the iron is transformed into ferric oxide which is not readily attacked by moist chlorine, and then subjected to the action of chlorine. The gold is thus converted into chloride which can be dissolved out in water, and metallic gold precipitated from the solution by the addition of reducing agents such as ferrous sulphate.

Potassium cyanide is now largely used for extracting gold, as it dissolves readily in this reagent.

The separation of silver and copper from gold may be effected by quartation. The success of this process, as the name implies, depends on the gold being present to the extent of not more than one-quarter of the mass of metal employed. The metal is boiled with strong sulphuric acid, converting the silver and copper into sulphates, so that on lixiviation with water these are dissolved and the gold left as a residue.

110. Properties.—Gold is a soft, orange-yellow metal of great brilliancy. Its physical characteristics render it very conspicuous among the metals; it is the heaviest of metals in common use with the exception of platinum, its specific gravity being 19.32. In malleability and ductility it surpasses all other metals; the former property is turned to advantage for the manufacture of gold leaf, for which purpose a bar of gold, containing 96.25 per cent. of gold, 2.5 per cent. of silver, and 1.25 per cent. of copper, is passed between rollers that extend it into the form of a broad ribbon; this is cut into squares that are packed between layers of fine vellum, and beaten with a heavy hammer; these thinner squares are then again cut up and beaten between layers of gold-beater's skin (made from

the intestine of the ox), until they are sufficiently thin. An ounce of gold may thus be spread over 100 square feet; 282,000 of such leaves placed on one another form a pile only 1 inch high. The gold leaves transmit green light, though when rendered non-lustrous by heat this light is ruby-red.

111. Although fusing at about the melting point of copper, gold is seldom cast, on account of its great contraction during solidification. Gold crystallizes in isometric forms, conducts heat and electricity well, and fuses at 1,061.7° C. It is unaltered in the air and is not attacked by any single acid or alkaline hydroxide, though solutions like aqua regia, that contain free chlorine, dissolve gold readily.

Gold is used both for jewelry and coinage. Being too soft alone for either purpose, it is alloyed with copper or silver, the mint alloy of the United States consisting of 9 parts of gold and 1 of copper. The purity of gold for jewelry is estimated by the carat, pure gold being 24 carats fine; hence, an alloy of 18 parts of gold to 6 of silver and copper is said to be 18 carats fine.

112. Gilding.—Gold is not even affected to the same extent as silver by exposure to the atmosphere, for hydrogen sulphide has no action on it, and hence it is better adapted than any other metal for coating surfaces that are required to preserve their luster.

Several processes are used for gilding metals such as silver and copper. The objects may be gilded by amalgamation or by electrodeposition. Gold readily alloys with mercury and the amalgam is used for gilding objects of silver and copper. The pieces to be gilded are heated to destroy greasy matter and are then cleaned by dipping them into dilute sulphuric acid, after which they are washed and dried with sawdust. They are then rubbed with a brush of brass wires dipped into a solution of mercurous nitrate, and then with a brush impregnated with an amalgam of 1 part of gold and 8 parts of mercury. They are afterwards heated to volatilize the mercury. The pieces thus gilded are dull, but become lustrous after suitable washings and polishings.

113. The best method of applying gold to other metals involves the electrodeposition of the gold. In this process the copper objects, which are previously heated and cleaned by dilute sulphuric acid, are plunged for a few seconds into dilute nitric acid and wiped dry. They are then connected with the negative pole of a battery and dipped into a bath composed of 1 part of cyanide of gold, 10 parts of potassium cyanide, and 100 parts of water. A plate of gold plunged into the same bath constitutes the positive pole. When the current passes the objects become covered with a uniform coating of gold. As the metal is precipitated from the solution, it is replaced by an equivalent quantity from that which constitutes the positive pole and which dissolves. The bath thus remains constant in composition. Best results are obtained when the solution is hot.

COMPOUNDS OF GOLD

114. Chlorides of Gold.—Auric chloride, $AuCl_3$, is formed when gold is dissolved in aqua regia, and if this solution is evaporated, the auric chloride is partly decomposed, with the formation of aurous chloride, $AuCl$. Auric chloride is formed also by passing chlorine gas through water containing finely divided gold in suspension. It melts at 288° C., when heated in a sealed tube. Auric chloride may be obtained in crystals containing 2 molecules of water of crystallization, $AuCl_3{\cdot}2H_2O$. When a solution of auric chloride is treated with stannous chloride, a purple precipitate known as purple of Cassius is formed. This appears to be metallic gold in a finely divided condition. When dry auric chloride is gently heated it is decomposed into chlorine and aurous chloride, and if this is treated with water it is decomposed into auric chloride and gold.

115. Oxides of Gold.—Three compounds of gold and oxygen are known, namely: Aurous oxide, Au_2O, auric oxide, Au_2O_3, and an auro-auric oxide, $(AuO)_4$.

Aurous oxide, Au_2O, is a violet-colored powder obtained when aurous chloride is treated with potassium hydroxide.

Hydrochloric acid forms metallic gold and the trichloride, thus:

$$3Au_2O+6HCl=2AuCl_3+3H_2O+4Au$$

Heated to 250° C., it decomposes into gold and oxygen. Sulphuric acid and nitric acid do not affect it.

Auric oxide, Au_2O_3, is obtained as a brown powder by gently heating auric hydroxide, $Au(OH)_3$, obtained by treating a hot solution of auric chloride with a hot solution of sodium hydroxide.

$$AuCl_3+3NaOH=Au(OH)_3+3NaCl$$
$$2Au(OH)_3+\text{heat}=Au_2O_3+3H_2O$$

Heat decomposes this oxide into metallic gold and oxygen. It is soluble in nitric acid. Potassium hydroxide dissolves it, forming potassium aurate, $KAuO_2$.

$$Au_2O_3+2KOH=2KAuO_2+H_2O$$

116. Sulphides of Gold.—Auric sulphide, Au_2S_2, is precipitated from a cold solution of a gold salt by hydrogen sulphide as a black or brownish-black mass which is accompanied by free sulphur. This sulphide is very unstable and forms soluble compounds when treated with alkaline sulphides.

Aurous sulphide, Au_2S, is precipitated as a steel-gray substance when a hot solution of a gold salt is treated with hydrogen sulphide. This sulphide dissolves in pure water and is reprecipitated from this solution by hydrochloric acid.

INORGANIC CHEMISTRY

(PART 10)

THE ALKALINE EARTH METALS

1. Introductory.—Early in the history of chemistry, the term *earth* was used by chemists to designate certain non-metallic substances which were only slightly soluble in water and which were refractory in character, that is, they did not decompose when subjected to the action of high temperatures. These substances were thought to be elementary in character until Davy, soon after his discovery of the alkalies potassium and sodium, showed that the so-called alkaline earths consisted of the oxides of the metals calcium, strontium, and barium. These oxides show increasing solubility and stronger alkalinity in the order named.

2. Calcium, strontium, and barium are not only very closely related to one another, but in some ways they are related to the members of the alkali group of elements, which have already been studied, and again in some ways to the rare earth group of metals which will be treated in this Section.

Two additional elements which will be studied in this Section and which are closely related to each other and, in some respects, to the alkaline earth metals, are magnesium and glucinum, the latter sometimes called beryllium.

The alkaline earth metals are the most important of those treated in this Section, and as calcium is the most abundant and important of these, it will be discussed first.

CALCIUM

Symbol Ca. Atomic weight 40.07

3. History and Occurrence.—Calcium carbonate and calcium sulphate were known to the ancients, the former being burned into lime for making mortar. It is from the Latin word for lime, *calx*, that the name calcium has been derived. The metal itself was discovered by Davy in 1808 and isolated in 1855 by Matthiessen, who obtained it by decomposing fused calcium chloride by means of the electric current. It is found abundantly in the mineral kingdom. As carbonate it forms the mineral calcite and the rock masses known as limestone, chalk, and marble. As sulphate, it forms vast beds of gypsum; as phosphate, it occurs as apatite; as fluoride, in fluorspar, etc. It also occurs as the phosphate in the bones of animals, in the shells of eggs and oysters, and in nearly all spring and river waters.

4. Preparation and Properties.—Metallic calcium may be obtained by the electrolysis of the fused chloride, or by heating an alloy of zinc and calcium to a high temperature to distil off the zinc and leave the calcium. The alloy is prepared by fusing together a mixture of calcium chloride, zinc, and sodium, when the sodium decomposes the chloride, and the calcium and zinc form an alloy; also, by the reduction of the oxide by heating with magnesium. Metallic calcium has a light-yellow, brilliant color, is about as hard as gold, and is very ductile and malleable. It oxidizes slowly in the air, though it is permanent in perfectly dry air. It decomposes water at ordinary temperatures. Its specific gravity is 1.57. The salts of calcium impart a brick-red tinge to an otherwise colorless flame.

COMPOUNDS OF CALCIUM

5. Calcium oxide, CaO, commonly known as lime or quicklime, is always prepared on a large scale by igniting limestone, which is impure calcium carbonate. If limestone or calcium carbonate is heated to 800° C. or over, dissociation

takes place and carbon dioxide, CO_2, a gas, is driven off and calcium oxide, CaO, or lime, remains. The reaction that takes place may be expressed as follows:

$$CaCO_3 + \text{heat} = CaO + CO_2$$

6. Common Lime Kilns.—The process of burning limestone is carried out in lime kilns of various types. The simple kind still used by farmers for burning limestone for agri-

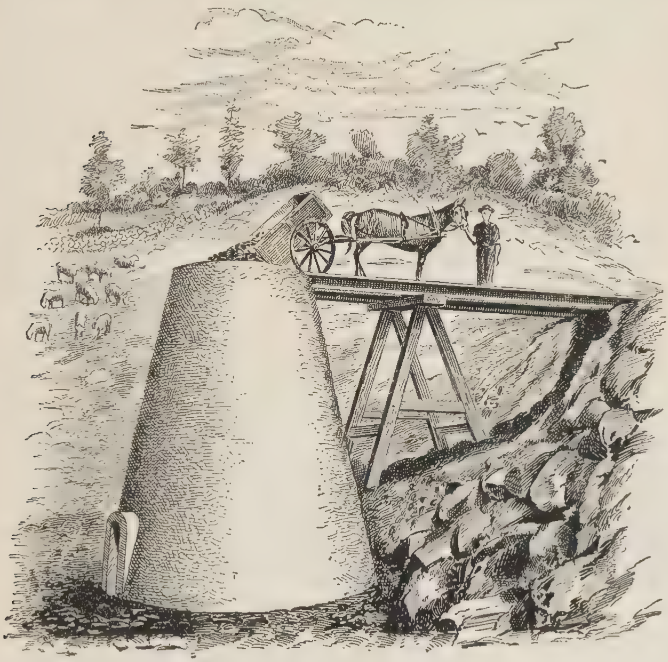


FIG. 1

cultural purposes, is constructed of stone and brick and located on a hillside, so that the top is readily accessible for charging the kiln with limestone and the bottom for drawing out the lime. The kiln itself consists merely of a pot-shaped structure with stone walls, and has a diameter of 8 or 10 feet at the top and a height of 15 or 20 feet.

As shown in Fig. 1, the stone is hauled over a platform built from the hill and dumped into the top of the kiln in which an

opening is left not only for charging but as an exit for the gases and smoke evolved during the process of burning. The charge, as the quarried limestone is called when placed in the kiln, rests on an arch built on the hearth with large pieces of limestone. It is piled up nearly to the top of the kiln, as shown in Fig. 2. The fire is built on the hearth, and lighted near the back, so that the heat will become more intense toward the mouth as the draft increases. The air that enters by the fire-door carries the flame to all parts of the arch and gradually brings the limestone to a state of white heat.

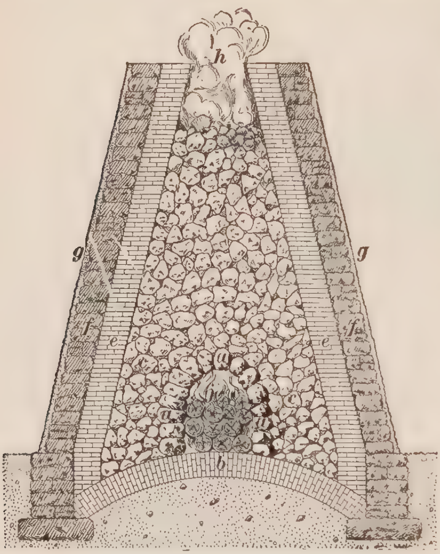


FIG. 2

7. In Fig. 2 is shown a section of the conical lime kiln as it was built in this country; *a* shows the limestone arch that rests on the firebrick hearth *b*, and under which the fire is built; *c* is the loose limestone thrown around and over the arch *a* and is composed of smaller pieces of rock; *e* is the inside firebrick lining of the kiln; *f* is the wall of the kiln itself, built of either stone or brick; *g* is the outside coating or plastering of clay put on to keep as much of the heat in the kiln as possible; *h* is the upper opening through which the kiln is charged and which also acts as a chimney for the escape of smoke, etc.; *j* is the wood fire that produces the necessary heat.

After kindling in this type of kiln the fire is allowed to burn until all the fuel is consumed, which requires several days, and after the contents of the kiln are sufficiently cool to handle the burned lime is drawn out. This process of burning is wasteful of fuel, owing to the amount used to heat up the kiln for each

burning; also, much time is lost in loading, heating, and cooling the charge.

8. **Continuous Lime Kilns.**—To do away with these objections, there are now in use what are known as continuous kilns in which the limestone and the fuel are charged into the kiln at the top and the burned lime is drawn out from time to time at the bottom, no cooling of the kiln being necessary. These kilns are lined with firebrick and are often from 25 to 30 feet high. Their greatest diameter at the middle is usually 8 or 10 feet, and at the top and at the bottom it is from 4 to 6 feet. The kilns mentioned in this and the preceding paragraphs are known as mixed-feed kilns, because the fuel and limestone are charged together at the top. These kilns give a product that is slightly contaminated by coal ash but good enough for most purposes. When a white lime is required, flame kilns are used. In this type the fuel and limestone do not come in contact with each other.

9. **Properties.**—Pure calcium oxide is a white, hard, amorphous substance having a specific gravity of about 3. It is a strong base, is non-volatile, and melts at approximately 2,570° C. in the electric furnace. On exposure to the air calcium oxide combines with the moisture of the air and crumbles. It absorbs water with great rapidity, forming the hydroxide and generating considerable heat. Calcium oxide is soluble in acids and slightly soluble in water, about 1 part in 800 parts of water.

10. **Calcium Hydroxide.**—Calcium hydroxide, $Ca(OH)_2$, generally known as slaked lime, hydrated lime, or calcium hydrate, is usually formed by adding water to the oxide, thus:

$$CaO + H_2O = Ca(OH)_2$$

It is a soft, white, bulky powder, and is slightly soluble in water, forming an alkaline, feebly caustic liquid known as lime water. Lime water readily absorbs CO_2 from the atmosphere, becoming milky, and precipitates $CaCO_3$. Calcium hydroxide is easily converted into calcium oxide by heat. It is widely used in industrial chemistry, being the cheapest alkaline substance.

11. Calcium Chloride.—Calcium chloride, $CaCl_2$, is produced by dissolving either calcium oxide or carbonate (chalk or white marble, for instance) in hydrochloric acid, and is frequently obtained as a waste product in the chemical industries, as in the manufacture of ammonia from ammonium chloride and quicklime:

$$2NH_4Cl + CaO = CaCl_2 + H_2O + 2NH_3$$

On evaporating an aqueous solution of calcium chloride, prismatic crystals having the composition $CaCl_2 \cdot 6H_2O$ are obtained. These crystals, $CaCl_2 \cdot 6H_2O$, lose 2 molecules of water when dried in vacuo, and the whole 6 molecules when heated above 200° C. The calcium chloride thus obtained, free from water, is used as a drying, or desiccating, agent in the laboratory, because of its great attraction for water. When calcium chloride is dissolved in water, heat is absorbed and the temperature of the solution is lowered and when this salt is mixed with snow or ice, temperatures as low as −48° C. may be obtained. Therefore, calcium chloride is used in freezing mixtures. A saturated solution of calcium chloride boils at 180° C., and is sometimes used in the laboratory as a convenient bath for obtaining a temperature above the boiling point of water. Calcium chloride is also used as a preservative, for fireproofing purposes and in the manufacture of sizing compounds.

12. Calcium Nitrate.—Calcium nitrate, $Ca(NO_3)_2$, is formed in nature in the vicinity of dwellings, in the soils of cellars, in damp walls, and as the anhydrous salt on the walls of stables and other places through which urine or other organic liquids percolate; it is frequently called lime saltpeter, or wall saltpeter. It may be prepared by treating calcium carbonate with nitric acid. The crystals have the formula $Ca(NO_3)_2 \cdot 4H_2O$, are deliquescent and soluble in water and alcohol. When heated and exposed to sunlight, calcium nitrate becomes luminous in the dark.

13. Calcium Carbonate.—Calcium carbonate, $CaCO_3$, occurs widely distributed in nature as the different varieties of limestone, marble, calcspar, and chalk. It is dimorphous, crys-

tallizing in rhombic crystals having a specific gravity of 3, as aragonite, and in hexagonal rhombohedra with a specific gravity of 2.7, as calcite.

Limestone and chalk are either amorphous or indistinctly crystalline calcium carbonate, while marble is a granular crystalline form. Oxides of iron and manganese are sometimes present in marble and give it a variegated appearance. When bituminous matter is present it is known as black marble.

Calcium carbonate is nearly insoluble in pure water. The presence of carbon dioxide in water increases its solubility. Heated to about 800° C., calcium carbonate decomposes into quicklime and carbon dioxide.

14. Calcium Sulphate.—Calcium sulphate, $CaSO_4$, occurs in nature in combination with 2 molecules of water as gypsum, $CaSO_4{\cdot}2H_2O$. It is also found in nature in the anhydrous condition as the mineral anhydrite. In combination with water this compound also forms transparent prisms known as selenite. By heating gypsum to between 150° and 200° C. it loses water and forms plaster of Paris, which when mixed with water combines with it and solidifies. When the gypsum is burnt it loses the equivalent of 1.5 molecules of water and forms the compound, $2CaSO_4{\cdot}H_2O$, which is called a hemihydrate and is generally known as plaster of Paris. This is more soluble than either the anhydrous salt or the salt containing 2 molecules of water, and part dissolves in the water and forms a saturated solution. The hydrate is thus formed and as the solution is supersaturated with respect to the hydrate, some of it crystallizes out in this form and the water thus released dissolves more of the hemihydrate. The process is thus repeated until the whole of the hemihydrate is converted into the hydrate. Plaster of Paris mixed with glue is frequently used for ornamental purposes under the name of stucco.

15. Precipitated calcium sulphate is used in the manufacture of paper, under the name of pearl hardener. Calcium sulphate is used in stables and farmyards for absorbing the ammonia of the decomposing animal excrements which would

otherwise be lost to the manure. It is contained in many natural waters and is one of the chief causes of permanent hardness. It is sparingly soluble in water so that the sulphates will precipitate calcium only from relatively strong solutions. The aqueous solution of $CaSO_4$ precipitates barium salts immediately, but strontium salts after an interval, on account of the greater solubility of $SrSO_4$. Calcium sulphate is most soluble in water having a temperature of 35° C.; 1 part of it then dissolves in 400 parts of water. It is insoluble in alcohol. Boiling HCl dissolves it and deposits it in needle-shaped crystals on cooling. It is used also as a filler for writing papers.

16. Calcium Fluoride.—Calcium fluoride, CaF_2, is found in nature as the mineral fluorspar. It occurs in small quantities in the bones and the enamel of the teeth, in the ashes of some plants, and in sea-water. It is insoluble in water and is only decomposed by strong acids. When heated it becomes luminous, fuses at a red heat, hence serves as a flux in the smelting of ores.

17. Calcium Sulphide.—Calcium sulphide, CaS, is obtained by heating calcium sulphate at a high temperature with charcoal. It is a yellowish-white mass that is luminous in the dark after having been exposed to the sunlight. This fact was first observed by Marggraf in 1750. Canton in 1768 described a method for obtaining the sulphide by strongly heating oyster shells with sulphur.

Calcium hydrosulphide, $Ca(SH)_2$, is obtained when a cream of calcium hydroxide is acted on by hydrogen sulphide. It crystallizes in colorless prisms with 6 molecules of water and readily melts in its water of crystallization. Warmed in a stream of hydrogen sulphide it decomposes into calcium sulphide and hydrogen sulphide.

Calcium sulphide forms the main constituent in the tank waste of the alkali works. A solution of calcium hydrosulphide is used in tanneries as a depilatory, or hair remover.

18. Calcium Phosphate.—Calcium phosphate, $Ca_3(PO_4)_2$, occurs in combination with calcium fluoride in the minerals

apatite and phosphorite. It forms approximately 80 per cent. of the ashes of all bones. Calcium phosphate is precipitated as a white gelatinous mass when disodium phosphate is added to an ammoniacal solution of calcium chloride. It is nearly insoluble in water but is soluble in hydrochloric acid, in nitric acid, and in acetic acid.

19. Primary Calcium Phosphate.—Primary calcium phosphate, $Ca(H_2PO_4)_2$, frequently called acid calcium phosphate, is prepared by the action of sulphuric acid on the normal phosphate. It is the chief constituent of the superphosphates used as fertilizers. It is prepared in the pure state by dissolving calcium phosphate in the required amount of phosphoric acid, and allowing the solution to evaporate when the salt crystallizes out in rhomboidal plates containing 1 molecule of water. It is readily soluble in water, and when heated changes to the metaphosphate, $Ca(PO_3)_2$.

20. Calcium Pyrophosphate.—Calcium pyrophosphate, $Ca_2P_2O_7$, is formed when secondary calcium phosphate, $CaHPO_4$, is strongly ignited. The secondary calcium phosphate is obtained as a precipitate when a solution of disodium phosphate is added to a solution of calcium chloride, which contains a little acetic acid.

$$(1) \quad CaCl_2 + Na_2HPO_4 = CaHPO_4 + 2NaCl$$
$$(2) \quad 2CaHPO_4 + \text{heat} = Ca_2P_2O_7 + H_2O$$

The acetic acid does not take part in the reaction but facilitates the formation of secondary calcium phosphate because of the insolubility of this compound in the acetic acid. The calcium pyrophosphate when heated to a red heat forms a perfectly transparent glass possessing all the properties of ordinary glass.

21. Calcium Silicates.—Calcium silicates are found associated with silicates of other metals in many minerals. They also enter into the composition of most glasses. Window glass, for instance, contains the silicates of calcium and sodium, and so-called Bohemian glass contains those of calcium and potassium.

STRONTIUM

Symbol Sr. Atomic weight 87.63

22. History and Occurrence.—Strontium was distinguished as a peculiar substance by Hope in 1792. Davy in 1808 recognized it as an elementary body, though it was not until 1855 that Bunsen and Matthiessen obtained it in the pure state. Strontium occurs in nature both as sulphate and as carbonate. The former, known as the mineral celestite (so called from the blue tint of many specimens), is mostly found in beautiful crystals associated with the native sulphur in Sicily; the latter is found in the mineral strontianite—derived from Strontian, Scotland, where it was first found, and from which the metal obtained its name strontium.

23. Preparation and Properties.—Metallic strontium is usually prepared by the electrolysis of its chloride, though it has been obtained by distilling strontium amalgam in hydrogen. The amalgam was prepared by the action of sodium amalgam on a saturated solution of strontium chloride.

Strontium is a pale-yellow metal of specific gravity 2.54; it is harder than lead, is malleable and ductile, and melts at 900° C. If heated in air, it burns vividly with a characteristic crimson flame. Though it is quite permanent in dry air, it decomposes water readily with the evolution of hydrogen.

COMPOUNDS OF STRONTIUM

24. Strontium Oxide.—Strontium oxide, or strontia, SrO, is, as a rule, obtained by igniting strontium nitrate, $Sr(NO_3)_2$. It is a grayish-white porous mass, is infusible, and unites energetically with water to form the hydroxide.

25. Strontium Dioxide.—Strontium dioxide, or peroxide, SrO_2, crystallizes in pearly plates containing 8 molecules of water when a solution of the oxide or hydroxide in water is treated with hydrogen peroxide. On being heated the anhydrous dioxide remains as a light white powder which gradually loses oxygen.

26. Strontium Hydroxide. — Strontium hydroxide, $Sr(OH)_2$, is obtained as the result of the union of strontium oxide and water. It is prepared on a large scale by heating celestite with brown hematite, $2Fe_2O_3{\cdot}3H_2O$, and coal dust.

$$4SrSO_4+2Fe_2O_3{\cdot}3H_2O+C=4Sr(OH)_2+4FeSO_4+CO_2 \\ +2H_2O$$

It forms colorless, deliquescent, quadratic crystals having the formula $Sr(OH)_2{\cdot}8H_2O$. It is more soluble in water than is calcium hydroxide, is used in sugar refining, and when strongly heated is converted into strontium oxide.

27. Strontium Nitrate.—Strontium nitrate, $Sr(NO_3)_2$, is prepared in considerable quantity by dissolving strontium carbonate—usually the mineral strontianite—in nitric acid. It is largely used in pyrotechnics to produce red fire. It is soluble in water, but insoluble in alcohol.

28. Strontium Chloride.—Strontium chloride, $SrCl_2$, crystallizes in needles having the composition $SrCl_2{\cdot}6H_2O$, and having a bitter taste. It is deliquescent and fairly soluble in alcohol, the alcoholic solution burning with a red flame.

29. Strontium Bromide.—Strontium bromide appears as transparent, colorless, hexagonal crystals; odorless, but with a bitter taste. It is deliquescent in moist air. The salt may be obtained by neutralizing dilute hydrobromic acid with strontium carbonate, evaporating and crystallizing.

30. Strontium Iodide.—Strontium iodide appears as transparent, colorless plates; in crystalline crusts, or in a white, granular powder; odorless and with a bitter, saline taste. It is deliquescent and becomes yellow, when exposed to air and light. The salt may be made by evaporating a solution of hydriodic acid saturated with strontium hydroxide or carbonate.

31. Strontium Carbonate and Sulphate.—The carbonate of strontium, strontianite, $SrCO_3$, and strontium sulphate, celestite, $SrSO_4$, are found in nature, as has been mentioned. They are insoluble in water, and are deposited as white precipitates on adding a soluble carbonate or sulphate

to the solution of a strontium salt. Strontium sulphate is, however, less soluble than calcium sulphate and more soluble than barium sulphate. Strontium salts impart a red color to a flame.

BARIUM

Symbol Ba. Atomic weight 137.37

32. History and Occurrence.—Barium was first recognized as a new element by Scheele in 1774. Davy, in 1808, succeeded in isolating the metal. Its name is derived from the Greek word *barys*, meaning heavy, because of the high specific gravity of all the barium compounds. It occurs in nature largely as the sulphate in heavy spar, or barite; as witherite, or barium carbonate, and in lead and silver ores.

33. Preparation and Properties.—Metallic barium is prepared by the electrolysis of the fused chloride, or by the electrolysis of the carbonate or sulphate mixed with mercury and mercuric oxide and distilling the amalgam.

Barium is a silver-white malleable metal with a specific gravity of 3.7, melts at 850° C., and boils at 950° C. It is stable in dry air but oxidizes rapidly in moist air, and decomposes both water and alcohol.

COMPOUNDS OF BARIUM

34. Barium Oxide.—Barium oxide, or **baryta,** BaO, is obtained by heating the nitrate. It is a heavy, gray, porous solid of specific gravity 5.5; it unites energetically with water, the action being accompanied by a hissing sound and the evolution of much steam. The product of the reaction, known as caustic baryta, is the hydroxide $Ba(OH)_2$, which is obtained according to the equation:

$$\underset{\substack{\text{barium}\\\text{oxide}}}{BaO} + \underset{\text{water}}{H_2O} = \underset{\substack{\text{barium}\\\text{hydroxide}}}{Ba(OH)_2}$$

Barium hydroxide is soluble in 2 parts of boiling water, and on cooling is deposited in large tabular crystals. The solution of barium hydroxide in water is known as baryta water.

35. Crystalline barium hydroxide may be prepared by adding powdered barium nitrate to a boiling solution of sodium hydroxide. The mixture is boiled for several minutes, filtered, and then slightly cooled, when crystals of undecomposed barium nitrate are deposited; and, if the clear liquid is poured off into another vessel and stirred, it deposits an abundant mass of crystals of barium hydroxide, having the composition $Ba(OH)_2 \cdot 8H_2O$. These crystals soon effloresce and become opaque when exposed to the air.

36. Barium Dioxide.—Barium dioxide, or peroxide, BaO_2, is obtained by passing dry oxygen over barium oxide heated to dull redness. It is a gray, sometimes green-appearing, porous substance, and loses its second atom of oxygen when heated to bright redness.

37. Barium Sulphide.—Barium sulphide, BaS, is obtained by reducing barium sulphate with charcoal, according to the equation:

$$BaSO_4+4C=BaS+4CO$$

or by passing hydrogen sulphide over heated barium oxide until no more water is formed.

Like calcium sulphide, it is phosphorescent. When dissolved in water, it is decomposed into barium hydroxide and barium hydrosulphide.

38. Barium Chloride.—Barium chloride, $BaCl_2 \cdot 2H_2O$, is the barium compound most used in the laboratory; it may be obtained by saturating the solution of barium carbonate with hydrochloric acid. Barium chloride is deposited in tabular crystals, belonging to the type of the orthorhombic prisms, which are unaltered in the air and have the formula $BaCl_2 \cdot 2H_2O$. It is easily soluble in water, but insoluble in alcohol, as well as in strong acids. It is poisonous.

39. Barium Chlorate.—Barium chlorate, $Ba(ClO_3)_2$, is of importance because of its employment in pyrotechnics. It is prepared by adding barium chloride to a solution of sodium chlorate. On concentration the sodium chloride crystallizes out first and is separated from the solution, which is then

evaporated and the chlorate purified by recrystallization. It crystallizes in shining, tabular prisms, with 1 molecule of water; it is readily soluble in water and alcohol. Mixed with sulphur and charcoal, and ignited it imparts a brilliant green color to the flame of the burning mixture.

40. Barium Nitrate.—Barium nitrate, $Ba(NO_3)_2$, is prepared by decomposing barium carbonate with dilute nitric acid, filtering and evaporating the solution. It crystallizes in regular octahedrons, the crystals being transparent and unaltered in the air. One part of barium nitrate requires for its solution about 20 parts of water at 12° C., 5 parts of water at 15° C., and 2.8 parts at 106° C. When heated to redness, barium nitrate gives off oxygen, nitrogen, and nitrogen dioxide, and is converted into barium oxide; thus,

$$2Ba(NO_3)_2 + \text{heat} = 2BaO + 2NO_2 + 3O_2 + N_2$$

Barium nitrate is used in the manufacture of explosives.

41. Barium Carbonate.—Barium carbonate, $BaCO_3$, occurs abundandantly in nature as the mineral witherite, in shining rhombic prisms. It is prepared as a dense white powder with a specific gravity of 4.3, by pouring a solution of barium chloride into an excess of a boiling solution of sodium carbonate. It is insoluble in water, and fuses at a white heat, losing carbon dioxide and forming the basic carbonate $BaO \cdot BaCO_3$.

42. Barium Sulphate.—Barium sulphate, $BaSO_4$, found abundantly in nature as barite, or heavy spar, has a specific gravity of 4.5. It is almost insoluble in water and acids, except in concentrated sulphuric acid, when the solution, on cooling, deposits crystals of acid barium sulphate, $BaH_2(SO_4)_2$. Artificial barium sulphate is used by painters instead of white lead, under the name of permanent white (blanc fixe), and as an adulterant of white lead. It is also employed for glazing paper, cards, etc., and is prepared by mixing the solution of a barium compound with dilute sulphuric acid, when the barium sulphate separates as a white precipitate which is collected, washed, and dried. The prepared barium sulphate has more body, or covering power, than the finely ground mineral.

REVIEW OF THE METALS OF THE ALKALINE EARTHS

43. Owing to their close relationship, calcium, strontium, and barium form a rather interesting natural group of metals. They exhibit a well-defined gradation in their attraction for oxygen; namely, barium is more readily tarnished or oxidized, even in dry air, than strontium, and strontium, again, more readily than calcium. The hydroxides of the metals exhibit a similar gradation in properties; barium hydroxide does not lose water, even when strongly heated, whereas the hydroxides of strontium and calcium are readily decomposed by a red heat. Barium hydroxide and strontium hydroxide are far more soluble in water than is calcium hydroxide, and they all exhibit a very decided alkaline reaction, which entitles them to the name of alkaline earths. Among the other compounds of these metals, the sulphates may be mentioned as presenting a gradation of a similar description; for barium sulphate may be considered insoluble in water, while strontium sulphate is slightly soluble, and calcium sulphate rather freely soluble.

GLUCINUM

Symbol Gl. Atomic weight 9.1

44. Occurrence.—Glucinum, also called beryllium, occurs in nature principally as a double silicate of glucinum and aluminum in the mineral *beryl*, which has the formula $Al_2Gl_3(SiO_3)_6$. It also occurs in the *emerald*, the composition of which is the same as beryl, but which is colored green by a little chromium, and in *chrysoberyl*, $Gl(AlO_2)_2$.

45. Preparation and Properties.—Glucinum is obtained by heating its chloride with metallic potassium or sodium, when the sodium or potassium unites with the chlorine and sets the glucinum free. It is a hard silver-white, ductile metal with a specific gravity of 1.85, melting at 1280° C. It is stable in the air, does not decompose steam at a red heat, and is strongly electropositive. When heated in a finely divided condition, it

burns in the air with great brilliancy. It is readily soluble in hydrochloric acid, but insoluble in nitric acid in the cold, and only slowly when warmed. Potassium hydroxide dissolves glucinum with the evolution of hydrogen.

COMPOUNDS OF GLUCINUM

46. When a soluble hydroxide is added to the solution of a glucinum salt, the hydroxide, $Gl(OH)_2$, separates as a white gelatinous precipitate that dissolves in an excess of the alkaline hydroxides with the formation of the corresponding glucinate.

$$(1) \quad 2\,NaOH + GlCl_2 = Gl(OH)_2 + 2NaCl$$

$$(2) \quad Gl(OH)_2 + 2NaOH = Na_2GlO_2 + 2H_2O$$

A large quantity of water decomposes these glucinates, and the hydroxide is again precipitated.

$$(3) \quad Na_2GlO_2 + 2H_2O = Gl(OH)_2 + 2NaOH$$

If the hydroxide is heated, water is given off and the oxide remains.

$$(4) \quad Gl(OH)_2 + \text{heat} = GlO + H_2O$$

Glucinum oxide, GlO, is a light, white, infusible powder that dissolves quite readily in either acids or alkalies, and is insoluble in water.

47. Glucinum chloride, $GlCl_2$, is prepared by heating a mixture of glucinum oxide with charcoal in a stream of chlorine.

$$2GlO + C + 2Cl_2 = 2GlCl_2 + CO_2$$

It may also be obtained by acting on the element with chlorine. It is deliquescent, and dissolves readily in water with the evolution of heat. When the solution in water is evaporated it crystallizes with 4 molecules of water.

48. Glucinum sulphate is formed by dissolving glucinum oxide, or better, the hydroxide, in dilute sulphuric acid. From a solution in water it crystallizes with 4 molecules of water, $GlSO_4{\cdot}4H_2O$. The crystals are readily soluble in water, have a sweet taste, and effloresce on exposure to the air. If a solution of the sulphate is heated with glucinum hydroxide, basic glucinum sulphates are formed.

The formation of glucinates from the hydroxide, the decomposition of the chloride when evaporated, and the formation of basic sulphates show that glucinum is a weak base and possesses acid properties.

MAGNESIUM

Symbol Mg. Atomic weight 24.32

49. History and Occurrence.—Magnesium carbonate, under the name of magnesia alba, has been known in Europe since the beginning of the 18th century, but, although Black in 1775 showed that this substance appeared to be a peculiar earth, its composition was not known until 1808 when Davy obtained the metal. The magnesium he obtained was rather impure; and not until 1830 by Bussy was it produced in an approximately pure form. Bunsen and Matthiessen in 1852 prepared it by electrolysis of fused magnesium chloride; and in 1857, Deville and Caron obtained it in large quantities by acting on the chloride with sodium, a process subsequently improved by Sonstadt.

Magnesium is found abundantly, as magnesite, $MgCO_3$; dolomite, $CaMg(CO_3)_2$; Epsom salts, $MgSO_4{\cdot}7H_2O$, etc. Among minerals containing this metal, those most frequently met with are certain combinations of silica and magnesia, well known by the names of talc, steatite, or French chalk, asbestos, and meerschaum; nearly all minerals containing magnesium possess a soapy feeling.

50. Preparation and Properties.—Magnesium may be prepared by the electrolysis of the chloride, but is more conveniently prepared by decomposing the chloride with sodium. In carrying out this process, magnesium chloride, fluorspar, and sodium are mixed and highly heated. As dry magnesium chloride is rather difficult to obtain, the double chloride of magnesium and potassium, $KMgCl_3$, is frequently substituted.

At the present time magnesium is prepared by the electrolysis of fused carnallite, $MgCl_2{\cdot}KCl{\cdot}6H_2O$. The carnallite is fused by external heat in a cylindrical steel vessel, which is made the cathode terminal. The anode is a carbon rod placed in a

porcelain cylinder through which a current of coal gas or hydrogen is passed to remove all the oxygen and chlorine evolved. The metal magnesium separates at the cathode and floats on the surface of the fused electrolyte.

Magnesium is a silver-white, brilliant metal having a specific gravity of 1.76. It is somewhat malleable and ductile, but is not very tenacious. It melts at 650° C., boils at 1,120° C., and may be obtained crystallized in regular octahedrons. It oxidizes readily in moist air, but is not attacked by dry air. Acids attack it with ease and it unites directly with most negative elements, including nitrogen. It burns when heated with an intense white light. It decomposes aqueous solutions of ammonium salts with an evolution of hydrogen, the double salt, magnesium ammonium sulphate, $MgSO_4 \cdot (NH_4)_2SO_4$, being formed, thus:

$$2(NH_4)_2SO_4 + 2H_2O + Mg = MgSO_4 \cdot (NH_4)_2SO_4 + H_2 + 2NH_4OH$$

The light produced by burning magnesium is particularly rich in chemically active rays, producing chemical changes similar to those caused by sunlight, so that photographs may be made by its means in the absence of sunlight.

COMPOUNDS OF MAGNESIUM

51. Magnesium Oxide.—Magnesium oxide, or magnesia, MgO, occurs in nature as the mineral periclasite crystallized in isometric forms; it is the sole product of the combustion of magnesium in the air, and is left whenever the carbonate, hydroxide, or nitrate of magnesium is ignited. It forms a soft, bulky, white powder that slowly attracts moisture from the air, to form the hydroxide, $Mg(OH)_2$. Magnesia is employed in medicine and in the manufacture of refractory lining for furnaces.

52. Magnesium Hydroxide.—Magnesium hydroxide, $Mg(OH)_2$, is found in nature as the mineral brucite. It is obtained as a white gelatinous mass when potassium or sodium hydroxide is added to a solution of a magnesium salt. It can be dried at 100° C. without decomposition, but is decomposed

into the oxide at a low red heat. It absorbs carbon dioxide from the air and is almost insoluble in water. It is used to a great extent in extracting sugar from sugar beets.

53. **Magnesium Chloride.**—Magnesium chloride, $MgCl_2$, is most readily prepared by igniting the double chloride of magnesium and ammonium; the ammonium chloride is thereby driven off and the magnesium chloride left as a white, translucent, crystalline mass, readily fusible and somewhat volatile. It is very soluble in water, and deliquesces readily. It may be prepared also by the action of hydrochloric acid on magnesium carbonate or oxide. It occurs in spring waters, sea-water, and in various salt beds. It has a saline, bitter taste.

54. **Magnesium Carbonate.**—Magnesium carbonate, $MgCO_3$, occurs in nature in rhombohedra, isomorphous with calcite, as the mineral magnesite. It also occurs combined with calcium carbonate as dolomite. It is present in nearly all natural waters, causing temporary hardness, the magnesium carbonate being precipitated by boiling. It is obtained as a white voluminous powder by drying the precipitate formed when an alkali carbonate is added to a solution of a magnesium salt. It has a bitter taste and an alkaline reaction. Magnesium carbonate is soluble in water containing carbon dioxide, but on boiling, it separates out in crystals containing 3 molecules of water.

55. **Magnesium Sulphate.** — Magnesium sulphate, $MgSO_4$, exists in solution in sea-water, and in certain purgative mineral waters, such as those of Epsom, in England, whence the name Epsom salt, so frequently applied to this substance. It also occurs as kieserite, $MgSO_4 \cdot H_2O$. It was formerly produced by heating dolomite and then treating the residue with sulphuric acid. It is now prepared by treating the crude kieserite on sieves with water, which dissolves the magnesium and sodium chlorides. The kieserite together with insoluble impurities is then removed from the sieves and is allowed to harden in conical wooden casks after which it is dried and powdered. In this state it contains from 80 to 90 per cent. of magnesium sulphate. It is then purified by crystallization.

Magnesium sulphate crystallizes in small, colorless prisms or needles, with 7 molecules of water, has a bitter, saline taste, and is soluble in water. The crystals fuse easily and lose 6 molecules of water at 150° C.; the last molecule of water can, however, be driven off only at a temperature of 200° C. or higher. From its intimate relationship to the compound, this last molecule of water is termed water of constitution.

Magnesium sulphate forms a series of double salts with the sulphates of the alkalies, of which the double sulphate of magnesium and potassium, $MgK_2(SO_4)_2 \cdot 6H_2O$, is an example.

56. Phosphates of Magnesium.—The normal orthophosphate, $Mg_3(PO_4)_2$, is contained in the bones of animals and in the seeds of cereals. It is obtained as a hydrated white precipitate having the formula $MgHPO_4 \cdot 7H_2O$, when disodium phosphate is added to the solution of magnesium salts.

Magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, is a frequent constituent of urinary calculi and is precipitated by disodium phosphate from ammoniacal solutions of magnesium salts. The precipitation is greatly accelerated by stirring. It is sparingly soluble in water, and nearly insoluble in ammonia. When heated it loses water and ammonia, forming magnesium pyrophosphate, thus:

$$2MgNH_4PO_4 \cdot 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O$$

THE ZINC, CADMIUM, AND MERCURY GROUP

INTRODUCTORY

57. This group consists of the metals zinc, cadmium, and mercury. The relationship between zinc and cadmium is much closer than between these two metals and mercury; they resemble magnesium quite closely, while in some ways mercury resembles the members of the Copper Group. Like magnesium, zinc and cadmium are bivalent, and form but one series of salts. Mercury, on the other hand, forms one series, known as mercurous salts, in which its valence appears to be 1, and another, known as mercuric salts, in which its valence is 2. Just as glucinum is a weak base, and shows acidic tendencies, so also zinc, the first member of the group under discussion, is a rather weak base, and exhibits acid tendencies, while the other members of the group do not. The hydroxides of glucinum and zinc dissolve in alkaline hydroxides, forming glucinates and zincates, while the hydroxides of the other members of this family are insoluble in alkaline hydroxides.

ZINC

Symbol Zn. Atomic weight 65.37

58. History and Occurrence.—Zinc occupies a high position among useful metals, being peculiarly fitted because of its lightness and durability for the construction of pipes, roofs, etc. An ore of zinc was used by the ancient Greeks, under the name cadmia, in the manufacture of brass. In Europe, zinc was first discovered in the 18th century, it having been until that time imported from China. The name zinc was given to the metal by Paracelsus in the 16th century.

The ores of zinc are found very abundantly in this country, in England, Transylvania, Hungary, and Silesia.

Metallic zinc as a rule does not occur free in nature, though it is claimed to have been found in the native state near Melbourne, Australia. The chief ores of zinc are calamine, $H_2Zn_2SiO_5$; smithsomite, $ZnCO_3$; the sulphide, zinc blende, ZnS; the oxide, zincite, or red zinc ore, ZnO; the silicate, willemite, $2ZnO \cdot SiO_2$; franklinite, $(ZnFe)O \cdot Fe_2O_3$; zinc spinel, or gahnite, $ZnO \cdot Al_2O_3$.

59. Preparation.—The preparation of metallic zinc even at the present time is not what may be exactly termed a successful metallurgical operation, since no matter what the process used on the ore some of the zinc is always lost during different stages of the operation. In a general way, most all commercially successful processes for the extraction and subsequent distillation of zinc may be described as follows: Depending upon their compositions, the ores are concentrated by mechanical or chemical methods or by the flotation process, as described for copper. The concentrates are then converted into zinc oxide by ignition in the case of a carbonate, and by roasting, if a sulphide. The oxide is then subjected to distillation, which is carried out under certain conditions.

60. In the Belgian process, the crushed oxide is mixed with from one-third to one-half its weight of powdered coal or coke placed in retorts and heated to about 1,400° C. The retorts are tube-shaped, made from fireclay, and are from 3 to 5 feet in length and from 6 to 10 inches in diameter. After being charged, a conical clay tube 18 inches long, called an adapter, is luted to the open end of the retort, and to this adapter is fitted a condenser of sheet iron, which catches any metal and also condenses the zinc fumes. The retorts are placed usually four deep in a large furnace holding from forty to sixty retorts, and fired by either coal, oil, or gas.

When the charge in the retorts approaches the temperature required for distillation, a fine gray powder, consisting of finely divided zinc with some zinc dust comes over first and is collected in an iron or earthenware receiver. This is then followed

by the liquid zinc. The product thus obtained is known to the trade as *spelter* and may contain arsenic, iron, lead, and cadmium as impurities.

61. Physical Properties.—Zinc is a bluish-white, highly crystalline metal; its specific gravity is about 7; its fracture is laminated and brilliant. It is hard and brittle at ordinary temperatures, and also at 200° C., but between 100° C. and 150° C. it is malleable and ductile and may be rolled into thin sheets. At 419° C. it melts, and at 918° C. it boils. When heated to redness in air, it volatilizes and burns with a greenish flame into a smoke of oxide that falls in bulky, white flakes, which were formerly known as flowers of zinc, or philosopher's wool. The metallurgy of zinc on a commercial scale depends at present entirely on the important fact that the metal is volatile when heated to a high temperature. The condensation of zinc vapor, however, is a matter requiring great care, for if diluted with even inert gases like nitrogen, it becomes more and more difficult to condense in a solid form, and finally, if the dilution be carried too far, nothing but a powder is produced. The temperature of condensation is also a matter of importance, and it is stated that effective condensation takes place only between 415° and 550° C.

62. Zinc alloys with a number of metals, the most important being copper, with which it forms the alloy known as brass. It may also contain a number of metals as impurities. Of these, however, only three are of sufficient frequence and effectiveness to be worthy of note—namely, cadmium, iron, and lead. Cadmium is a very frequent impurity, because of its nature which is closely allied to zinc; cadmium ores are nearly always found with zinc ores. Cadmium hardens zinc somewhat, but since, as a rule, it is found in very small quantities, its effects are rarely injurious. Iron is also frequently present, and may be retained in considerable quantities, but is usually removed by a process of refining before zinc is put on the market. If present to an extent greater than 1 per cent., it interferes with the properties by virtue of which zinc may be rolled into sheets, and is also injurious in zinc that is to be utilized for the desilverization of

lead. Galena, or sulphide of lead, is frequently associated with zinc ores, and the two metals are extremely difficult to separate; in fact, no process for their complete separation has been put in successful operation. The amount of zinc that can be held in solution by lead increases with the temperature of the molten lead; the percentage of lead retained by molten zinc varies in exactly the same manner. Lead is removed from zinc by a process of refining before being marketed. In general, its effect is to make zinc soft.

63. The great strength of iron has been ingeniously combined with the resistance of zinc to oxidization in the so-called galvanized iron. This is manufactured by coating clean iron sheets with melted zinc, thus affording a much needed protection in and around large towns, where the oxides of sulphur arising from the combustion of coal, and the acid emanations from various factories greatly accelerate the corrosion of unprotected iron. The iron plates to be coated are at first thoroughly cleaned and then dipped into a vessel of melted zinc, the surface of which is covered with sal ammoniac (ammonium chloride), in order to dissolve the zinc oxide that forms on the surface of the metal and that might adhere to the iron plate, thus preventing its becoming uniformly coated with the zinc. A coat of zinc which adheres more firmly is obtained by first depositing a thin film of tin on the surface of the iron plate by galvanic action, whence the name galvanized iron is derived.

64. Chemical Properties.—Although zinc stands high in the scale of metals as arranged with respect to their electropositive or negative qualities—that is, nearer to the alkali-metals end of the scale than copper or iron, for instance—it is not readily oxidized by air or water at ordinary temperatures. In the presence of carbon dioxide, water, and water vapor, it becomes coated with basic carbonate of zinc, which protects it from further change. Upon heating in air or in a current of steam, the power to take up oxygen becomes much greater and at red heat, some steam is decomposed. As has been seen, zinc vapor burns very readily, and it is even possible to burn

the metal before volatilization takes place. Zinc is attacked by most acids, although when pure it is less readily attacked then when impure. This is probably due to the fact that its solution by acids causes the evolution of hydrogen, which acts as a protective film if the zinc be pure. If impure, an electric couple is formed between the zinc and the metal forming the impurity, and on account of the electropositive quality of zinc, the impurities almost invariably constitute the negative pole and the hydrogen is consequently liberated at that pole. Zinc is also soluble in solutions of caustic alkalies and water, and some types of electric cells are made dependent on this property. Heated in contact with carbon monoxide, no action takes place. Heated in contact with carbon dioxide, zinc is partially converted into zinc oxide, ZnO, with a corresponding partial decomposition of the carbon dioxide into carbon monoxide and the oxygen necessary to form the oxide of zinc.

COMPOUNDS OF ZINC

65. Zinc Oxide.—Zinc oxide, ZnO, occurs in nature as red zinc ore, or zincite. It is the sole product of the combustion of zinc in the air, and is also prepared by heating the carbonate or nitrate. It is used under the name of zinc white as a stable white paint, and is also used in medicine. It is prepared for medicinal purposes by igniting the basic carbonate $2ZnCO_3 \cdot 3Zn(OH)_2$, which is precipitated by treating a solution of zinc sulphate with sodium carbonate. Thus:

$$5Zn\,SO_4 \cdot 7H_2O + 5Na_2CO_3 \cdot 10H_2O = 2ZnCO_3 \cdot 3Zn(OH)_2 + 5Na_2SO_4 + 3CO_2 + 82H_2O$$

$$2ZnCO_3 \cdot 3Zn(OH)_2 + \text{heat} = 5ZnO + 2CO_2 + 3H_2O$$

It is an amorphous white powder, becoming a lemon yellow when hot, has a specific gravity of 5.78, absorbs carbon dioxide from the air, is insoluble in water but soluble in dilute acids, ammonium hydroxide, and ammonium carbonate. Heated in the oxyhydrogen flame, it emits a brilliant white light. When used as a paint it has the advantage over white lead of being harmless to the health of the users, and is not affected by

hydrogen sulphide. It has a greater tendency, however, to crack and peel off than the white lead paint.

66. Zinc Hydroxide.—Zinc hydroxide, $Zn(OH)_2$, is obtained as a gelatinous precipitate when caustic alkalies are added to solutions containing zinc, thus:

$$ZnSO_4+2KOH=K_2SO_4+Zn(OH)_2$$

The precipitate dissolves in an excess of alkali, and, if this be not too great, it is reprecipitated by boiling. Zinc hydroxide is readily decomposed by heat, thus:

$$Zn(OH)_2=ZnO+H_2O$$

67. Zinc Sulphide.—Zinc sulphide, ZnS, is found crystallized in nature, forming the mineral sphalerite, or blende. It is generally yellowish brown in color, has a resinous luster, and is translucent. It is precipitated from zinc solutions by alkali sulphides as a white precipitate, easily soluble in acids. The natural sulphide is easily converted into the sulphate by roasting it in the air.

68. Zinc Chloride.—Zinc chloride, $ZnCl_2$, is prepared in the laboratory by dissolving zinc in hydrochloric acid, or by acting on the metal with chlorine. If zinc is dissolved in hydrochloric acid and the solution is concentrated by evaporation, crystals having the composition $ZnCl_2 \cdot H_2O$ are deposited. If these are heated to expel the water, or if the original solution is evaporated to dryness, the chloride is partly decomposed with the formation of the basic chloride and the hydroxide of zinc. The anhydrous chloride has a strong affinity for water and is sometimes used as a desiccating agent; it is a white, granular powder, of specific gravity 2.9, melts at a little over 262° C., and is soluble in water and alcohol. It is used on a large scale for the weighting of cotton goods, the preservation of timber, and externally in medicine as an antiseptic. A solution having a specific gravity of 1.7 and containing an excess of the oxide will dissolve silk.

69. Zinc Sulphate.—Zinc sulphate, $ZnSO_4$, crystallizes from an aqueous solution with 7 molecules of water as $ZnSO_4$

$\cdot 7H_2O$. The crystals are rhombic prisms. As with magnesium sulphate, six of these molecules of water are quite easily expelled by heat, while the seventh is driven off only with difficulty.

Zinc sulphate is prepared by dissolving zinc in sulphuric acid and, on a large scale, by the careful roasting of blende at a low red heat. It is known as white vitriol, is colorless, has an astringent, metallic taste, effloresces in dry air, and is somewhat soluble in water. It is used in pharmacy and in the dye industry.

70. Zinc Acetate.—Zinc acetate occurs as soft, white, six-sided, monoclinic plates with a pearly luster. Its odor is faintly acetous, and a dilute solution has a metallic taste.

The acetate may be produced by submitting zinc oxide to the action of acetic acid.

71. Zinc Carbonate.—Zinc carbonate is a white, odorless, and tasteless powder; it is insoluble in water or in alcohol, but soluble in diluted acids.

It is produced by the interaction of zinc sulphate and sodium carbonate, resulting in a solution of sodium sulphate with a precipitate of zinc carbonate, which quickly passes to the basic carbonate.

72. Manufacture of Lithopone.—When solutions of barium sulphide and zinc sulphate are brought together in the proportions indicated by the equation

$$BaS + ZnSO_4 = BaSO_4 + ZnS$$

a heavy flocculent precipitate of barium sulphate and zinc sulphide is obtained. This mixture is extensively used in the manufacture of paints, but before it is suitable for this purpose it must be subjected to further treatment. The precipitate obtained as described is filtered, washed, dried, heated to a dull redness, and, while hot, is plunged into water. It is then thoroughly ground with the water and then washed and dried, when it is ready for the market.

73. The heating of the mixture of zinc sulphide and barium sulphate produces no chemical change, but its physical

characteristics are completely changed. Thus, before ignition, the precipitate is unfit for use as a paint pigment, as it possesses no body or covering power. After ignition, however, it is obtained as a fine, pure white powder which is superior to zinc oxide in covering power. Lithopone is extensively used in the manufacture of enamel and marine paints and in the oil-cloth industry.

CADMIUM

Symbol Cd. Atomic weight 112.4

74. History and Preparation.—Cadmium was discovered in 1817 by Hermann, and also by Strohmeyer, the latter giving to it the name cadmium, from *cadmia*, the ancient name of zinc ore; it is generally found associated with zinc, and also as the sulphide in the mineral greenockite. It occurs as an impurity in commercial zinc from which it is separated by dissolving the alloy in dilute hydrochloric acid and precipitating the cadmium as the sulphide by passing hydrogen-sulphide gas through the solution. Zinc is not precipitated.

$$CdCl_2+H_2S=CdS+2HCl$$

The cadmium sulphide so obtained is then dissolved in hot concentrated HCl and ammonium carbonate is added to the solution whereby cadmium carbonate is obtained; thus:

$$CdCl_2+(NH_4)_2CO_3=CdCO_3+2NH_4Cl$$

The cadmium carbonate is then purified by washing, dried, and strongly heated, the oxide being formed as follows:

$$CdCO_3+\text{heat}=CdO+CO_2$$

Upon distilling the oxide with carbon, the metal is obtained, thus:

$$2CdO+C+\text{heat}=2Cd+CO_2$$

75. Properties.—Cadmium resembles zinc, its compounds being analogous to those of this metal, but it is whiter, heavier, and more easily volatilized and more fusible than zinc. It is ductile and malleable at ordinary temperatures, but becomes brittle at about 82° C., and if bent when in this condition, it

crackles like tin. It has a specific gravity of 8.7 and melts at 320° C. It is not attacked by air, but acids act on it slowly. At red heat it burns, producing brown fumes of cadmium oxide. Cadmium differs from all other metals in forming a yellow sulphide insoluble in alkalies, so that its salts, mixed with excess of ammonia and treated with H_2S, give a yellow precipitate. Cadmium is used in the preparation of alloys of low melting point.

COMPOUNDS OF CADMIUM

76. Cadmium Oxide.—Cadmium oxide, CdO, may be obtained by calcining either cadmium carbonate or nitrate. Its color varies from yellowish brown to dark brown. It is reduced at high temperatures by carbon and by hydrogen, its reduction taking place more readily than that of zinc oxide.

77. Cadmium Sulphide.—Cadmium sulphide, CdS, occurs in nature as greenockite in the form of bright-yellow, hexagonal prisms, terminated by six-sided pyramids. It is prepared in the laboratory by precipitating a solution of cadmium salt with hydrogen sulphide or a soluble sulphide, an amorphous precipitate of a fine yellow color being thus obtained.

78. Cadmium Iodide. — Cadmium iodide, CdI_2, is obtained by digesting finely divided cadmium with iodine in the presence of water. It crystallizes from its aqueous solution in transparent, hexagonal prisms having a brilliant luster. It is soluble in water and alcohol, melts at 385° C., and gives off iodine when heated to a higher temperature. Cadmium iodide, as well as cadmium bromide, $CdBr_2$, is used in photography.

79. Cadmium Sulphate.—Cadmium sulphate, $CdSO_4$, is obtained by dissolving either the metal, its oxide, or its carbonate in dilute sulphuric acid. The crystalline compound has the formula, $3CdSO_4 \cdot 8H_2O$.

80. Cadmium Chloride.—Cadmium chloride, $CdCl_2$, crystallizes from solution of the metal or oxide in hydrochloric

acid in rectangular prisms having 2 molecules of water. These readily effloresce in the air, lose water on heating, melt at 568° C., and sublime at a higher temperature.

MERCURY

Symbol Hg. Atomic weight 200.6

81. **History and Occurrence.**—Mercury has been known from the earliest times; its Latin name *argentum vivum*, of which the English name quicksilver is a literal translation, refers to its fluidity as well as to its color. The name mercury, from the planet of that name, was given by the alchemist to all volatile substances, but only this one has retained it. The symbol of mercury, *Hg*, is derived from the Latin name *hydrargyrum*. It occurs native only sparingly, the chief ore being the sulphide, called cinnabar, which is found principally in Idria, Austria; Almaden, Spain; and New Almaden, California.

82. **Preparation.**—The process of extracting the mercury from its ore is a rather simple and easy one. It usually consists in roasting the ore in a reverberatory furnace or even in a small blast furnace with access of air, by which the sulphur is oxidized to sulphur dioxide and the mercury set free and volatilized, according to the equation:

$$HgS+O_2=Hg+SO_2$$

Sometimes lime or oxide of iron is mixed with the ore, and the sulphur retained in this way as sulphide of calcium or iron, depending on which has been used. The condensation of the vapors of mercury is, however, a matter of some difficulty, and the methods employed vary considerably in different localities.

At Idria the vapors are passed through chambers and a series of twin tubes of cast iron cooled externally by water. They are so arranged that the condensed metal collects and runs down into the receptacle at the base of each tube. In Almaden, twelve parallel series of conical clay receivers, called aludels, luted together, are interposed between the furnace and

its flue; each of these is about 20 inches long, and a series extends about 20 yards. The lines of aludels are of sufficient length to allow the vapors and gases to cool nearly to the temperature of the air, and are so arranged as to allow the condensed mercury to gravitate toward a common channel where it collects.

83. Properties.—Mercury is a brilliant, silver-white metal. It has a specific gravity of 13.59 at 0° and is the only metal that is liquid at the ordinary temperatures. Cooled to −38.8° C., it solidifies to a malleable, tin-white mass, which is easily cut. Even at ordinary temperatures mercury has a small vapor tension, and constantly gives off minute quantities of its vapor into the atmosphere when exposed in an open vessel. It boils at 357° C., yielding a colorless vapor of specific gravity 6.976. When heated almost to its boiling point in air, it becomes coated with the red oxide, HgO. It is unaltered in air; neither hydrochloric nor dilute sulphuric acid attacks it, but boiling, strong sulphuric acid, and even dilute nitric acid, dissolve it readily. Chlorine and sulphur unite directly with it.

84. Mercury is used in the industries for filling thermometers and barometers, and very extensively for extracting gold and silver from their ores. With most of the metals it forms alloys, known as amalgams; in some cases these amalgams possess a definite composition and crystalline form, for example, Hg_6Na is brittle and crystallizes in regular forms. Sodium amalgam is a convenient reducing agent, for when brought into contact with water or solutions in water, hydrogen is evolved. Tin amalgam is sometimes used for producing the silver coating on glass for mirrors.

Mercury forms two series of compounds, the mercurous, in which this metal is monovalent, and the mercuric, in which it is divalent. It should be noted that the two series differ very considerably in properties.

COMPOUNDS OF MERCURY

85. Mercurous Oxide.—Mercurous oxide, Hg_2O, is a dark-brown or black powder obtained by adding a solution of potassium or sodium hydroxide to a solution of a mercurous salt; thus,

$$2HgCl + 2NaOH = Hg_2O + 2NaCl + H_2O$$

It is very unstable, and is decomposed by the action of light or heat into mercuric oxide and metallic mercury.

86. Mercuric Oxide.—Mercuric oxide, HgO, may be prepared by either a dry or a wet method. The first consists in decomposing mercuric nitrate by heat; the salt is gradually heated in a flask in a sand bath until vapors cease to be disengaged. The oxide thus prepared is an orange-red, granular, and crystalline powder. It may also be prepared by heating mercury in air for some time. By the wet method, mercuric oxide is prepared by decomposing a solution of a mercuric salt by potassium hydroxide, a yellow precipitate of mercuric oxide being thus obtained.

When mercuric oxide is heated, it assumes a dark-red color and decomposes, if the temperature is above 400° C., into oxygen and mercury. Mercuric oxide is soluble in acids, yielding mercuric salts. Hydroxides of mercury are unknown.

87. Mercuric Sulphide.—Mercuric sulphide, HgS, occurs in nature as the mineral cinnabar, both massive and in red rhombohedral crystals. It is obtained artifically by direct synthesis. The combination takes place when the elements are triturated in the cold, in the proportion of 100 parts of mercury and 18 parts of sulphur. A black mass is thus obtained that is sublimed in iron vessels. The black sulphide may be obtained also by treating a mercuric salt with H_2S. It becomes red when sublimed.

The pigment vermilion is a finely divided mercuric sulphide having a beautifully rich scarlet color. It is prepared by triturating for several hours, in a mortar, 300 parts of mercury and 114 parts of flowers of sulphur, and adding to the black

sulphide thus obtained 75 parts of potassium hydroxide and 400 parts of water. The mixture is maintained at a temperature of about 45° C., being continually triturated with a pestle. As soon as the powder has acquired a fine scarlet color, it is rapidly washed with hot water and dried. It is employed in the manufacture of paints, and in coloring sealing wax, and for various other purposes.

88. Mercurous Chloride.—Mercurous chloride, $HgCl$, ordinarily called calomel, is precipitated whenever a chloride is added to a solution of a mercurous salt. It occurs in nature in tetragonal prisms in the mineral horn quicksilver. Commercially, it is prepared by subliming a mixture of mercuric sulphate, mercury, and salt:

$$HgSO_4+Hg+2NaCl=Na_2SO_4+2HgCl$$

The heavy yellowish-white powder that condenses is washed with water to remove any mercuric chloride. It is not soluble in water, though chlorine water and nitric acid dissolve it by converting it into mercuric chloride. It sublimes between 400° and 500° C. without melting. Calomel is gradually decomposed by light, and is blackened by ammonium hydroxide.

89. Mercuric Chloride.—Mercuric chloride, $HgCl_2$, also known as bichloride of mercury, and as corrosive sublimate, may be obtained by heating mercury in chlorine. It is manufactured by heating dry mercuric sulphate with an equal quantity of dry salt. A small amount of manganese dioxide is usually added to the mixture to prevent the formation of calomel. The mixture is placed in large glass vessels and heated, when the corrosive sublimate is converted into a vapor and condenses on the cooler part of the vessel in a white, transparent, or lustrous crystalline mass. It has an acrid, persistent, metallic taste, melts at 265° C., sublimes at 300° C., and is somewhat soluble in water and in alcohol. It is used for the preservation of anatomical specimens, for dressing furs and skins, and as an antiseptic in surgery.

Mercuric chloride is a violent poison. Its antidote is the white of an egg, this forming an insoluble compound with the

poison, thus rendering it inert to the stomach. Mercuric chloride unites with a number of other chlorides, forming readily soluble double salts. It also unites with mercuric oxide, forming oxychlorides.

90. Mercurous Iodide.—Mercurous iodide, HgI, is, as a rule, prepared by direct synthesis, 100 parts of mercury and 63.5 parts of iodine being triturated until the whole is converted into a green powder, which is then washed with boiling alcohol and dried. It may also be obtained by precipitating a mercurous salt with potassium iodide. Mercurous iodide is a rather unstable compound, being decomposed by light as well as by heat, the latter decomposing it into mercury and mercuric iodide. The same decomposition is effected by potassium iodide and the alkaline chlorides.

91. Mercuric Iodide.—Mercuric iodide, HgI_2, is prepared by pouring a solution of 100 parts of potassium iodide into a solution of 80 parts of corrosive sublimate, $HgCl_2$. A scarlet-red precipitate of mercuric iodide is thrown down. It is absolutely necessary that the compounds be mixed in exactly the proportions given; an excess of potassium iodide would dissolve the mercuric iodide first precipitated.

Mercuric iodide is nearly insoluble in water; it is slightly soluble in boiling alcohol which deposits the mercuric iodide on cooling in small, red, octahedral crystals.

On heating to 254° C., mercuric iodide melts to a dark-yellow liquid that solidifies, when cooled, to a yellow mass. At 349° C. the liquid boils and its vapor condenses to a dark-yellow liquid that solidifies to a yellow mass; at the same time, right rhombic prisms of a yellow color sublime. If these are rubbed with a glass rod or other hard substance, they instantly become red, first at the point of contact, then throughout the entire mass.

Mercuric iodide with potassium iodide forms a compound that is soluble in water. A solution of this potassium mercuric iodide is not precipitated by potassium hydroxide, but the liquid rendered alkaline by the latter compound is a very sensitive test for ammonia (Nessler's test), with which it gives

a precipitate or a brown cloud more or less intense, according to the quantity of ammonia present.

92. Sulphates of Mercury.—A mercurous sulphate, Hg_2SO_4, and a mercuric sulphate, $HgSO_4$, are obtained by heating together mercury and sulphuric acid, the particular one formed depending on whether an excess of mercury or sulphuric acid is used. The mercuric sulphate is the more important salt. It consists of white crystals that, on heating, undergo decomposition with the formation of mercurous sulphate. In presence of water the salt is very liable to become basic.

93. Nitrates of Mercury.—Mercurous nitrate, $HgNO_3$, and mercuric nitrate, $Hg(NO_3)_2$, are formed from mercury and nitric acid under similar conditions to the sulphates, and, like them, form basic salts in the presence of water. For the weaker acids the affinity of mercury is too feeble to admit the formation of stable salts; the phosphates, carbonates, borates, and silicates have either not been prepared at all, or are obtained as basic compounds of variable composition.

BORON-ALUMINUM GROUP

94. Introductory.—The important members of the boron-aluminum group are the elements boron and aluminum. Members of lesser importance and which may be classed as rare metals are scandium, yttrium, lanthanum, ytterbium, and others, whose position in the periodic table has not yet been established because of insufficient investigation. A general resemblance exists between the different members of this group, but there is a gradation in properties from those of low to those of higher atomic weight. As was said in the discussion of the members of the nitrogen-phosphorus group, the lighter members, nitrogen and phosphorus, are decidedly acidic or non-metallic in character, while the heaviest member of the group, bismuth, is basic or metallic. The same thing is noticeable in the boron-aluminum group. Boron, the lightest member of the group, is almost devoid of basic properties, and must be classed as a non-metal; aluminum, the second member, has

both acid and basic properties, but as both are weak and the basic properties appear to predominate, it is usually considered as a metal. The other members have higher atomic weights and are more strongly basic.

BORON

Symbol B. Atomic weight 10.9

95. History and Occurrence.—Boron occurs almost exclusively in the mineral kingdom, but it is claimed that it has been found in grape vines and in a few other plants. It is not found in the free state in nature but in combination, as borax, or tincal, $Na_2B_4O_7 \cdot 10H_2O$; boracite, $2Mg_3B_8O_{15} \cdot MgCl_2$; borocalcite, $CaB_4O_7 \cdot 4H_2O$; natroborocalcite, $Na_2B_4O_7 \cdot 2CaB_4O_7 \cdot 18H_2O$, and sassolite, or boric acid, H_3BO_3.

Under the Arabic name *buraq* (corrupted into borax), a salt obtained from certain lakes in Thibet which contains boron as an essential constituent, has been imported into Europe for a long time, and has been used in medicine, in working metals, and in imitating precious stones.

From this borax Homberg in 1702 obtained boron trioxide from which Davy in 1807 by utilizing electricity, and Gay-Lussac and Thenard in 1808 by chemical processes, obtained pure boron. Wöhler and Deville succeeded in 1856 in crystallizing it. The mineral sassolite is boric acid, H_3BO_3; and borax, boracite, and ulexite are natural borates of sodium, magnesium, and calcium, respectively.

96. Preparation and Properties.—Boron possesses two distinct forms—amorphous and crystalline. Amorphous boron is obtained by heating boron trioxide with potassium. The boron thus obtained is a greenish-brown powder, of specific gravity 2.45, that burns with a green flame at 700° C., and is a rather poor conductor of electricity. It is readily oxidized by nitric acid and is infusible at the temperature of the oxy-hydrogen flame.

The crystalline variety is obtained either by dissolving the amorphous modification in melted aluminum, when boron crys-

tallizes out upon the aluminum cooling or by melting boron trioxide and aluminum together and subsequently treating the mixture with hydrochloric acid to remove the impurities such as aluminum and carbon from the crucible. Boron crystallizes in short yellow or brownish-yellow quadratic octahedrons with a specific gravity of 2.65. The luster and hardness of crystallized boron is next to that of the diamond and it will scratch both corundum and the ruby. The crystalline modification of boron is infusible and is insoluble in any acid. Aqua regia attacks it slowly. It is slowly soluble in melted caustic soda or potash.

Heated to 410° C. in chlorine, boron forms boron trichloride. Heated to redness, boron absorbs nitrogen, forming a white, infusible, insoluble powder of boron nitride, BN.

HALOGEN COMPOUNDS OF BORON

97. Boron Trichloride.—Boron trichloride, BCl_3, may be obtained by heating crude amorphous boron in a current of chlorine, or by passing dry chlorine over a strongly heated mixture of boron trioxide and charcoal, according to the equation:

$$B_2O_3+3C+3Cl_2=2BCl_3+3CO$$

In a pure state, boron trichloride is a colorless, highly refractive liquid of specific gravity 1.35 at 17° C., boils at 12.5° C., and fumes in the air. It is readily decomposed by water into boric and hydrochloric acids:

$$BCl_3+3H_2O=3HCl+B(OH)_3$$

98. Boron Tribromide.—Boron tribromide, BBr_3, is obtained either by direct combination of its constituents or by passing bromine vapor over a heated mixture of charcoal and boron trioxide. It is a strongly fuming, colorless liquid, specific gravity 2.65, that boils at about 90° C. Its vapor is colorless and it is decomposed by water the same as the trichloride.

99. Boron Trifluoride.—Boron trifluoride, BF_3, was discovered by Gay-Lussac and Thenard in 1810. It is prepared by heating an intimate mixture of boric oxide and finely

powdered calcium fluoride with sulphuric acid; the gas evolved is collected over mercury. The occurring reaction may be expressed by the equation:

$$3CaF_2+B_2O_3+3H_2SO_4=3CaSO_4+3H_2O+2BF_3$$

Boron trifluoride is a colorless gas having an extremely suffocating odor; it fumes in the air and condenses to a liquid at $-101°$ C.; it is decomposed by water and must, therefore, be collected over mercury. Its affinity for water is so great that it carbonizes paper and certain organic substances in the same way as does strong sulphuric acid. Potassium and sodium burn brilliantly when heated in it.

The solution of boron fluoride in water is accompanied by a chemical reaction that is shown when the aqueous solution of this gas, saturated at ordinary temperatures, is cooled to 0° C., for crystals of boric acid are deposited, and a very acid liquid, fluoboric acid, HBF_4, formed, according to the equation:

$$4BF_3+3H_2O=3HBF_4+B(OH)_3$$

BORON AND OXYGEN

100. Boron Trioxide.—Boron trioxide, B_2O_3, is formed whenever boron burns in air or oxygen. It is usually obtained by igniting boron hydroxide, or boric acid, $B(OH)_3$. A viscid mass is left, which solidifies to a colorless, transparent, and brittle glass having a specific gravity of 1.83. It unites readily with water, volatilizes at a white heat, and in a molten condition it dissolves nearly all metallic oxides.

101. Boric Acid.—Boric acid, $B(OH)_3$, or H_3BO_3, was discovered by Homberg in 1702. It occurs free in nature in volcanic districts, as in Tuscany, where it issues, mixed with steam and gaseous matter, from fissures in the earth into natural or artificial little lakes or ponds, known as lagoons, or lagoni. The gases (suffioni) contain sensible traces of boric acid, which is dissolved by the water of the lagoni, which soon becomes charged with the acid; on evaporation this water furnishes the crude boric acid. Boric acid may be prepared from sodium borate or borax by dissolving it in boiling water,

adding sulphuric acid, and allowing the whole to cool. The boric acid separates out in white, crystalline scales that are somewhat greasy to the touch and have a specific gravity of 1.43. They are soluble in 30 parts of water at 18° C., and freely soluble in alcohol, the latter solution burning with a greenish flame. The aqueous solution of boric acid is feebly acid; it changes blue litmus solution to a wine color and turns turmeric paper brown. This constitutes the normal or orthoboric acid. When heated to 120° C., it loses 1 molecule of water and is converted into metaboric acid, HBO_2. If the latter is maintained for some time at a temperature of 140° C., it is converted into tetraboric acid, $H_2B_4O_7$, according to the equation:

$$4HBO_2 = H_2B_4O_7 + H_2O$$

Borax occurs naturally in the waters of certain lakes and marshes in California and Thibet. It is largely used as a flux in working metals.

ALUMINUM

Symbol Al. Atomic weight 27.1

102. History and Occurrence.—Aluminum is one of the most abundant and at the same time most widely distributed constituents of the earth's crust. It derives its name from the word alumen, meaning alum. For a long time alumina, or aluminum oxide, was confounded with lime, from which it was first distinguished by Marggraf in 1754. In 1826 Oersted first prepared the chloride, and Wöhler, in 1828, obtained the metal from this salt. This process was made a commercial one by St. Claire Deville in 1854. Aluminum does not occur free in nature. It is found, as nearly pure aluminum oxide, in corundum, ruby, and sapphire; in diaspore, $AlOOH$; in bauxite, $Al_2O(OH)_4$; in feldspar, $K_2Al_2SiO_6$; in cryolite, Na_3AlF_6; and as a silicate in all clays and in many minerals.

103. Preparation.—Aluminum was first produced commercially by the process invented by St. Claire Deville, which consists in reducing the chloride with sodium. By an improvement in this method sodium aluminum chloride, cryolite, and

sodium are mixed together and heated in a furnace. A violent action takes place, great heat is evolved, and the liquefied mass of slag and metal gathers in the furnace. The latter is drawn off and cast into ingots. Tissier, at Amfreville, France, makes aluminum from the mineral cryolite after a method proposed by H. Rose; and in the United States it is now produced in considerable quantities from the same mineral by electrolysis, a process devised by Hall.

The Hall electrolytic process for the preparation of aluminum has almost entirely superseded the first-mentioned process. In this process pure anhydrous aluminum oxide is dissolved in a bath of fused cryolite and fluorspar in an iron pot, lined with carbon, which forms the cathode. The anode is composed of one or more carbon rods. The bath is kept at a temperature of about 1,000° C. The aluminum oxide is reduced, the metallic aluminum falling to the bottom of the pot, while the oxygen unites with the carbon of the anode. The fluoride remains unchanged; hence, by frequently withdrawing the metal and renewing the aluminum oxide, the process is made continuous.

104. Properties and Uses.—Aluminum is a white metal with a somewhat bluish luster when polished. It crystallizes in octahedrons, and is a good conductor of heat and electricity. It is ductile, malleable, highly sonorous, and very light, its specific gravity being 2.5 to 2.7. It is less fusible than tin and zinc but more so than silver, its fusing point being 657° C. It requires a very high temperature to vaporize it. Like zinc it is most easily rolled and bent between 100° and 150° C.

Aluminum is unaltered by the air, even by moist air. When heated in thin sheets in a current of oxygen, it burns and is converted into aluminum oxide. Nitric and sulphuric acids scarcely attack it. Hydrochloric acid dissolves it readily, disengaging hydrogen; it is also immediately attacked by boiling solutions of potassium or sodium hydroxide, the hydrogen being disengaged and alkaline aluminates formed.

105. The remarkable lightness of this metal renders it extremely useful in the manufacture of beams of chemical

balances, and of small weights, such as the decigram, centigram, and milligram, since these weights when made of aluminum are more than three times as large as those of brass, and nearly nine times larger than when made of platinum; also, the relative indestructibility of aluminum by the fumes of acids adds still more to the value of weights made from this metal. The metal is also now extensively used in the manufacture of cooking utensils, and especially of canteen vessels for military purposes, where, on account of its lightness and ability to resist vegetable acids, it has proved itself extremely useful. Aluminum, in the form of powder, is a powerful reducing agent, the combination with oxygen being accompanied by an enormous elevation of temperature. It can be used for reducing from their oxides metals—such as chromium and tungsten—that are difficult to reduce by other means. The great heat produced by burning aluminum powder is used for welding iron and steel. Other important applications of metallic aluminum are as conductors of the electric current and in the preparation of various alloys, especially those used in dirigible balloon and airplane construction. The chief impurities of the commercial aluminum are traces of iron and silicon.

COMPOUNDS OF ALUMINUM

106. Aluminum Oxide.—Aluminum oxide, Al_2O_3, generally known as *alumina*, occurs in nature in the mineral corundum, which includes the precious stones known as the ruby and sapphire, as well as the valuable polishing material called *emery*, distinguished by its extreme hardness, in which it ranks next to the diamond. It may be prepared by the combustion of the metal in oxygen or by igniting the hydroxide. Fusion with potassium bisulphate or with caustic potash renders it soluble in acids.

107. Aluminum Hydroxide. — Aluminum hydroxide, $Al(OH)_3$, also called alumina, occurs in nature as hydrargillite, or gibbsite, or as diaspore, $AlOOH$. These two modifications are crystalline. It is prepared by adding ammonium hydroxide to the solution of a salt of aluminum, when a gelatinous pre-

cipitate separates. This is nearly insoluble in an excess of ammonium hydroxide, but is readily soluble in potassium and sodium hydroxides. When washed and dried, the gelatinous hydroxide shrinks very much, and forms a mass resembling gum.

Aluminum hydroxide may be used in the preparation of lakes, which are insoluble colored compounds made by precipitating dyestuffs from their solutions by the addition of aluminum hydroxide. It and aluminum acetate are also used as mordants in dyeing. The fabric to be dyed is first treated with aluminum hydroxide or acetate and then with a solution of the dye, which is precipitated upon the cloth as an insoluble compound.

108. Aluminum Chloride.—Aluminum chloride, $AlCl_3$, sometimes written Al_2Cl_6, is prepared by passing over an incandescent mixture of alumina and charcoal a current of chlorine, aluminum chloride and carbon monoxide being formed according to the equation:

$$Al_2O_3+3C+3Cl_2=3CO+2AlCl_3$$

The aluminum chloride thus obtained is a white, semi-crystalline, waxy substance, having sometimes a light-yellow color; it is fusible, and volatilizes in the air at a temperature slightly above 100° C. When exposed to the air, aluminum chloride gives off white fumes and readily attracts moisture. It dissolves in water with the production of heat. A solution of aluminum chloride may be obtained by dissolving gelatinous alumina in hydrochloric acid. When this solution is evaporated, it decomposes as soon as it attains a certain degree of concentration, disengaging hydrochloric acid and leaving aluminum oxide. Aluminum chloride readily combines with sodium chloride, forming a double chloride, $NaAlCl_4$.

Authorities differ as to the molecular weight of aluminum chloride, but recent experiments tend to show that at high temperatures or when taking part in chemical reactions the formula is $AlCl_3$, while at lower temperatures it is Al_2Cl_6.

109. Aluminum Sulphate. — Aluminum sulphate, $Al_2(SO_4)_3$, is obtained by dissolving aluminum hydroxide in

dilute sulphuric acid. It crystallizes with difficulty in needles and in thin pearly scales, in which state it contains 18 molecules of water of crystallization; it dissolves in 2 parts of cold water, and has a sweet, astringent taste. When slowly heated, it first loses its water of crystallization until at a higher temperature it gives off sulphur trioxide, leaving a residue of alumina, according to the equation:

$$Al_2(SO_4)_3 = 3SO_3 + Al_2O_3$$

Aluminum sulphate is used as a mordant in dyeing, for the treatment of sewage, and for weighting of paper.

110. Alums.—By the term *alum* is ordinarily meant potassium aluminum sulphate, or potassium alum, $Al_2(SO_4)_3 K_2SO_4 \cdot 24H_2O$. This compound is obtained as a crystalline deposit by adding to a concentrated solution of potassium sulphate a concentrated solution of aluminum sulphate and stirring the mixture well with a glass rod. It is only slightly soluble in cold water, but dissolves more easily in hot, and quite abundantly in boiling water, being deposited from the latter on cooling, in voluminous, transparent octahedrons, and has a specific gravity of 1.7. When heated, these crystals melt in their own water of crystallization; in losing this water the melted mass swells considerably.

111. Alum may also be obtained crystallized in cubes. It is prepared in this form near Civita Vecchia, Italy, by working a mineral that contains the elements of alum with a large excess of alumina; this mineral is known as aluminite, and the cubical alum is known as Roman alum. This cubical variety may be prepared in the laboratory by adding a small quantity of potassium carbonate to a hot solution of ordinary alum, so that the precipitate first formed will be redissolved on agitating the liquid; on cooling, cubical, opaque crystals are deposited. These are formed under the influence of a small quantity of basic sulphate (aluminum sulphate combined with an excess of alumina) contained in the liquid, and which probably enters into the constitution of the crystals. With this slight difference, octahedral and cubical alum represent the same composition.

112. Ammonium Alum.—Ammonium alum is obtained by adding ammonium sulphate to a solution of aluminum sulphate. It possesses a composition analogous to that of ordinary alum, with which it is isomorphous. Its formula is $Al_2(SO_4)_3(NH_4)_2SO_4{\cdot}24H_2O$. It is very often substituted in the industries for potassium alum, because it is cheaper than the latter. When strongly calcined, it leaves a residue of pure alumina.

Other alums are known, in which iron, manganese, and chromium play the part taken by aluminum in ordinary alum. The most important of these compounds are: ammonium chromium alum, $Cr_2(SO_4)_3(NH_4)_2SO_4{\cdot}24H_2O$; ammonium iron alum, $Fe_2(SO_4)_3(NH_4)_2SO_4{\cdot}24H_2O$; potassium chromium alum, $Cr_2(SO_4)_3K_2SO_4{\cdot}24H_2O$; potassium iron alum, $Fe_2(SO_4)_3K_2SO_4{\cdot}24H_2O$; and potassium manganese alum, $Mn_2(SO_4)_3K_2SO_4{\cdot}24H_2O$.

113. Mineral Silicates of Aluminum.—The silicates of aluminum occur in combination with silicates of other elements in large quantities in the crust of the earth. Aluminum is very frequently replaced by iron in the form of Fe_2O_3, thus rendering the chemical formulas of these minerals rather complicated. The chief silicates of aluminum are: Topaz, $Al_2SiO_4F_2$; garnet, $(Mg{\cdot}Fe)_3Al_2Si_3O_{12}$; orthoclase, $Al(Si_3O_8)K$; kaolin, $H_2Al_2Si_2O_8{\cdot}H_2O$; and albite, $NaAl(Si_3O_8)$.

RARE METALS OF THE BORON-ALUMINUM GROUP

SCANDIUM

Symbol Sc. Atomic weight 44.1

114. Occurrence and Properties.—Scandium is found in the rare minerals, gadolinite and euxenite. Its compounds resemble those of aluminum. Its oxide, known as scandia, has the formula Sc_2O_3; the metal itself has not been isolated. It is infusible and insoluble in alkalies. Like aluminum, scandium forms a sulphate $Sc_2(SO_4)_3$, a double sulphate $KSc(SO_4)_2$, and other salts resembling those of aluminum. It is somewhat more basic than aluminum, however.

YTTRIUM

Symbol Yt. Atomic weight 89.33

115. Occurrence and Properties.—Yttrium like scandium is found in gadolinite and euxenite. It is also found in samarskite, a North Carolina mineral, and in some other rare minerals. The metal may be obtained by electrolyzing a solution of the chloride, $YtCl_3$, or by fusing the chloride with sodium. Its hydroxide, $Yt(OH)_3$, is obtained by treating a solution of one of its salts with potassium hydroxide. The hydroxide thus formed is not dissolved by an excess of the potassium hydroxide. Yttrium hydroxide is more basic than aluminum hydroxide. It unites with the carbon dioxide of the air to form a carbonate. The oxide, Yt_2O_3, is obtained by heating the hydroxide or nitrate. The chloride is easily obtained and crystallizes with 6 molecules of water, $YtCl_3 \cdot 6H_2O$.

LANTHANUM

Symbol La. Atomic weight 139

116. Occurrence and Properties.—Lanthanum also occurs in gadolinite, but is more abundant in cerite, a mineral of the same type and also containing the metal cerium. It is prepared almost exclusively from cerite by treatment with nitric acid, treatment with sodium hypochlorite, and fractional crystallization. It is a white, malleable metal with a specific gravity of 6.16, and melts at 810° C. Heated in the air, it forms the oxide, La_2O_3, and nitride, LaN. The oxide has a specific gravity of 6.5, and combines with water with the evolution of heat, forming the hydroxide, $La(OH)_3$.

YTTERBIUM

Symbol Yb. Atomic weight 173.5

117. Occurrence and Properties.—Ytterbium is found in gadolinite and euxenite. Its compounds have the same form as those of aluminum and resemble those of yttrium in properties. Its hydroxide, $Yb(OH)_3$, is insoluble in alkaline hydroxides and unites with carbon dioxide. It forms an oxide, Yb_2O_3, and other compounds which are colorless.

GADOLINIUM AND SAMARIUM

118. Occurrence and Properties.—Gadolinium, *Gd*, atomic weight 157.3, and samarium, *Sm*, atomic weight 150.4, are found in the minerals samarskite, gadolinite, cerite, and some others. They appear to form compounds like those of aluminum, and are generally classed in this group. The oxide of gadolinium, Gd_2O_3, is white and the salts are colorless. Metallic samarium has a white color, it melts at 1,350° C., has a specific gravity of 7.7, and tarnishes readily. It forms light-yellow salts and usually acts as a trivalent element, although a chloride having the formula $SmCl_2$ has been prepared. This chloride forms a reddish-brown mass soluble in water. The

chloride, $SmCl_3$, crystallizes in large yellow tablets having 6 molecules of water.

119. Other elements whose position in the periodic system is not definitely known, and which are obtained from the rare earths are: Holmium, *Ho*, atomic weight 163.5; erbium, *Er*, atomic weight 167.7; and thulium, *Tm*, atomic weight 168.5. All these are obtained from the same source as yttrium. All form some salts that show absorption bands, but very little is known regarding these elements.

THE GALLIUM-INDIUM-THALLIUM GROUP OF RARE ELEMENTS

120. Introductory.—This group consists of the three rare elements, gallium, indium, and thallium. Gallium is trivalent in most of its compounds, but also forms compounds in which it is bivalent. The principal compounds of indium are those in which the element is trivalent, but it also forms bivalent compounds. Thallium acts as a monovalent and trivalent metal in its compounds.

GALLIUM

Symbol Ga. Atomic weight 70.1

121. History, Occurrence, and Preparation.—Gallium was discovered in 1875 by Lecoq de Boisbaudran in a zinc blende from the mine of Pierrefitte in the valley of Argeles, Pyrenees, in France; its name is derived from Gallia, the Latin name of France. It is prepared by treating the ore with acids and the solution is decomposed by means of zinc. The precipitate is treated with hydrochloric acid and a precipitate again thrown down by means of zinc. The solution is then saturated with hydrogen sulphide, the precipitate filtered off, and the excess of hydrogen sulphide removed from the solution by boiling. The solution is next neutralized with sodium carbonate, then made slightly acid with dilute sulphuric acid, and boiled when the basic sulphate of gallium is precipitated. This precipitate is dissolved in sulphuric acid, the solution is

mixed with acid ammonium acetate, again saturated with hydrogen sulphide, and filtered. The filtrate is diluted with water, heated to boiling and filtered. This precipitate is dissolved in the required amount of sulphuric acid, is neutralized with potassium hydroxide and a slight excess added, and then electrolyzed, the gallium being deposited on the cathode, from which it is easily removed by bending the cathode under cold water.

122. Properties.—Gallium is a tough, grayish-white metal that can be cut with a knife. It melts at 30.1° C., and has a specific gravity of 5.9. When melted it has the color of silver and remains liquid for a long time, even when cooled to 0° C. Heated in the air, it is only slightly oxidized, is not volatile at a red heat, and is soluble in acids and alkalies.

123. Compounds of Gallium. — Gallium hydroxide, $Ga(OH)_3$, is precipitated as a white flocculent substance by the action of the alkali hydroxides. It is readily soluble in excess of the precipitant, but difficultly soluble in ammonia.

The oxide, Ga_2O_3, is obtained by igniting the nitrate. If this is heated in hydrogen part of it is volatilized and the rest appears to be converted into GaO. By treating gallium with chlorine the two chlorides $GaCl_2$ and $GaCl_3$ are formed. The chlorides are both decomposed by the action of water, forming basic chlorides, and finally gallous chloride, $GaCl_2$, is completely decomposed with the formation of the oxide.

Gallic sulphate is crystalline and deliquescent. Boiling water converts it into a basic salt. With ammonium sulphate it forms an alum, $GaNH_4(SO_4)_2 \cdot 12H_2O$, that is analogous to ammonium alum.

INDIUM

Symbol In. Atomic weight 114.8

124. Indium was discovered by Reich and Richter in 1863 in a specimen of zinc blende from Freiberg, Saxony, by means of the spectrum. It is prepared by dissolving the zinc made from the Freiberg ore, and which contains about .1 per cent. of indium, in either hydrochloric or sulphuric acid,

care being taken to leave an excess of zinc. When the acid has been used up, the solution is allowed to stand over the excess of zinc, on which the indium is then slowly deposited. This deposit is dissolved in nitric acid, and any impurities, such as lead and iron, introduced with the zinc are subsequently removed. The lead is separated as the sulphate, and the indium and iron precipitated with ammonium hydroxide. This precipitate is dissolved in hydrochloric acid, and boiled for some time with sodium bisulphite, thus precipitating indium sulphite. This is converted into the sulphate by boiling with nitric and sulphuric acids, and the metal precipitated with zinc.

It is a white, malleable metal, resembling lead, and dissolves readily in hydrochloric and sulphuric acids. Its specific gravity is 7.11. Its fusing point is 155° C., and it burns with a violet light and a brown smoke, producing the oxide. It is at ordinary temperatures unaltered in the air, and produces a gray streak on paper. It does not tarnish in the air or in boiling water.

125. Compounds of Indium.—Indium hydroxide, $In(OH)_3$, results as a gelatinous precipitate when an indium solution is treated with sodium or potassium hydroxide. It is soluble in an excess of the reagent. When the hydroxide is heated, the oxide, In_2O_3, results.

The chloride, $InCl_3$, results from the action of chlorine on the metal. The sulphate, $In_2(SO_4)_3$, is formed by dissolving the metal in sulphuric acid; it combines with ammonium sulphate to form the alum, $InNH_4(SO_4)_2 \cdot 12H_2O$. Though the term alum is usually applied to one substance, the term in its broadest sense means a double sulphate of a monad and triad, with 12 molecules of water of crystallization.

THALLIUM

Symbol Tl. Atomic weight 204

126. Thallium was discovered by means of the spectroscope in the flue dust of a sulphuric-acid works in the Harz Mountains. It imparts a bright-green color to a flame and obtained its name from a Greek word meaning a green branch.

It may be obtained in the metallic state by adding zinc to a solution of the sulphate. It is a bluish-white metal resembling lead. It is oxidized when heated in air and is somewhat malleable, but not ductile. Its specific gravity is about 11.8, and its fusing point is about 302° C. It decomposes water at a red heat, is readily soluble in nitric and sulphuric acids, but less soluble in hydrochloric acid. It forms two classes of salts.

127. Compounds of Thallium.—Thallous hydroxide, $TlOH$, is obtained by the action of air and water on the metal, or by treating the solution of the sulphate with barium hydroxide. It dissolves readily in water, and forms an alkaline solution.

Thallic hydroxide, $Tl(OH)_3$, is formed by adding potassium hydroxide to a thallic solution. When dried this loses water and $TlO \cdot OH$ remains.

Thallous oxide, Tl_2O, is formed by heating thallous hydroxide in such a way that oxidation is avoided. It is a black powder, melting at 300° C.

Thallic oxide, Tl_2O_3, is obtained by burning the metal in oxygen.

Thallous chloride, $TlCl$, is formed by treating the metal with chlorine, or it may be obtained as a white curdy precipitate by adding hydrochloric acid to a thallous solution. This precipitate turns violet when exposed to light. By suspending thallous chloride in water, and passing a current of chlorine through it, thallic chloride, $TlCl_3$, is formed.

Thallous sulphate, Tl_2SO_4, is formed by the action of sulphuric acid on the metal. It unites with the sulphates of the triads forming **alums**; as, for example, $AlTl(SO_4)_2 \cdot 12H_2O$.

Thallic sulphate, $Tl_2(SO_4)_3$, unites with sulphates of the alkalies, forming double salts, but these do not crystallize like the alums.

In general it may be said that in the thallous condition thallium acts like the alkalies, and in the thallic condition it acts like aluminum.

INORGANIC CHEMISTRY
(PART 11)

CARBON, SILICON, AND RELATED ELEMENTS

GENERAL DISCUSSION

1. The carbon-silicon group consists of the elements carbon, silicon, germanium, tin, and lead. The element carbon has already been treated in a preceding Section.

The relationship of the members of the carbon-silicon group will be more clearly understood if it is remembered that it has already been shown that carbon with an atomic weight of 12.005 possesses the characteristics of a non-metal and forms an acidic oxide, CO_2. Silicon with an atomic weight of 28.3 also forms oxides which are acidic, but in some of its physical properties it resembles the metals. Germanium, atomic weight, 72.5, may be classed as both a metal and a non-metal. The oxide, GeO_2, unites with acids to form salts and also with the alkalies, forming germanates, which are analagous to the silicates.

Tin, atomic weight, 118.7, also exhibits acid and basic properties, but the latter are more marked than is the case with germanium. Lead, atomic weight, 207.2, shows increasing basic properties over the other elements of this group.

2. The elements of the carbon-silicon group may be divided into two sub-groups, in so far as their physical and chemical properties are concerned, one consisting of carbon and silicon, and tin and lead in the other, germanium remaining as the connecting link.

Thus, carbon and silicon exist in different allotropic forms, which are similar in many respects. Both unite with hydrogen and oxygen to form the analogous compounds CH_4, SiH_4, CO_2, and SiO_2, respectively.

Carbon and silicon are very resistant to the action of high temperatures. Thus, the former has never been melted and the latter only at temperatures higher than 1,420° C.

Tin and lead possess the physical properties of true metals and, like germanium, they form two series of compounds in which the element is divalent and tetravalent.

SILICON

Symbol Si. Atomic weight 28.3

3. History and Occurrence.—Silicon was first obtained pure by Berzelius in 1825. It does not occur free in nature but is found abundantly in combination with oxygen, forming such well-known substances as quartz and flint. In combination with oxygen and various metals, such as aluminum and potassium, it constitutes a large portion of the rock formations that compose the solid crust of the earth.

4. Preparation and Properties.—Silicon may be obtained by the action of sodium on potassium fluosilicate:

$$K_2SiF_6+4Na=2KF+4NaF+Si$$

The silicon thus obtained is a brown powder (amorphous silicon) that resists the action of all acids, except hydrofluoric, by which it is attacked, forming silicon tetrafluoride and evolving hydrogen:

$$Si+4HF=SiF_4+2H_2$$

It may also be dissolved by a solution of potassium hydroxide, with the evolution of hydrogen and the formation of potassium silicate, K_2SiO_3.

$$Si+2KOH+H_2O=K_2SiO_3+2H_2$$

Though silicon burns brilliantly when heated in oxygen it does not burn completely owing to the fact that it becomes coated with silicon dioxide, SiO_2, which is fused by the intense

heat of the combustion. When heated with the blowpipe on platinum foil it eats a hole through the metal, with which it forms the fusible platinum silicide.

5. If potassium fluosilicate is fused with aluminum a portion of the latter combines with the fluorine while the remainder combines with the silicon, forming aluminum silicide. By boiling this with hydrochloric acid and then with hydrofluoric acid, the aluminum is extracted and crystalline scales of silicon possessing a metallic luster resembling that of black lead, are left. These crystalline scales are known as graphitoid silicon. In this shape silicon does not burn in oxygen nor is it soluble in hydrofluoric acid; in a mixture of nitric and hydrofluoric acid, however, it is soluble. Though amorphorus silicon is a non-conductor of electricity, the crystalline variety, like graphite, readily conducts it. The amorphous variety may through an extremely intense heat be transformed into the incombustible and insoluble form. It seems appropriate to remark that the combustibility of amorphous carbon (charcoal) is also diminished to a considerable extent after exposure to a high temperature.

Silicon is capable of being fused at a temperature somewhat above the melting point of cast iron; on cooling, it forms a brilliant metallic-looking mass which may be obtained by certain processes, crystallized in octahedrons, whose hardness is so great that they scratch glass like diamond.

6. In their chemical relations to other substances a considerable analogy exists between silicon and carbon. Silicon, however, is capable of displacing carbon as, for instance, if potassium carbonate is fused with silicon, potassium silicate is formed, and carbon separates. Silicon further resembles carbon in its disposition to unite with metals and to form compounds that retain their metallic luster; it unites directly with zinc, platinum, and aluminum, forming compounds that resemble metallic alloys. Nitrogen enters into combination with silicon directly at high temperature.

SILICON TETRAHYDRIDE

Formula SiH_4. Molecular weight 32.332

7. Preparation.—Silicon tetrahydride may be prepared by decomposing magnesium silicide with hydrochloric acid:

$$3Mg_2Si+12HCl=6MgCl_2+SiH_4+Si_2H_6+H_2$$

The magnesium silicide is first prepared by heating together to a very high temperature powdered sand or quartz, which consists largely of silicon dioxide, with magnesium powder; thus,

$$SiO_2+2Mg=Mg_2Si+O_2$$

8. Properties.—Silicon tetrahydride is a colorless gas which at $-1°$ C. under a pressure of 100 atmospheres is condensed into a liquid which under normal pressure, boils at $-112°$ C. It is insoluble in water. When mixed with hydrogen it is spontaneously inflammable in air, yielding white clouds of silicon dioxide. Burned from a jet, the gas gives a brilliant white flame that deposits a layer of brown silicon upon a disk or plate of porcelain held in it. When the tube conveying the gas is heated, a mirror-like deposit of silicon is formed within the tube. Passed into cupric sulphate or silver nitrate it precipitates cupric and silver silicide, Cu_2Si and Ag_4Si, respectively.

SILICON HEXAHYDRIDE

Formula Si_2H_6. Molecular weight 62.648

9. Preparation.—The equation representing the formation of silicon tetrahydride also shows that the compound Si_2H_6 or silicon hexahydride is formed at the same time. This compound is also a gas and may be separated from silicon tetrahydride by first liquefying the gases and then fractionally distilling the liquid obtained. Silicon hexahydride is a colorless gas which boils at $-15°$ C. under normal pressure. The solid obtained by freezing the liquid, by means of liquid air, melts at $-132.5°$ C.

SILICON DIOXIDE, OR SILICA

Formula SiO_2. Molecular weight 60.3

10. Occurrence.—The only oxide of silicon known, silicon dioxide, or silica, is found widely distributed in nature as quartz, opal, flint, sand, etc. It occurs also in combination with bases in the form of silicates, as asbestos, mica, soapstone, cement, glass, etc. Its purest form is the transparent and colorless variety known as quartz, which crystallizes in the hexagonal system and has a specific gravity of 2.6. When colored a delicate purple the crystals are known as amethysts. When its transparency and crystalline structure are lost and it is colored with iron oxide, it becomes chalcedony and carnelian.

11. Preparation and Properties.—Silica may be prepared either by the oxidation of silicon, as when it burns in the air, or by the dehydration of silicic acid:

$$H_2SiO_3 - H_2O = SiO_2$$

Silicon dioxide in the form in which it is usually obtained is a white amorphous powder, though in nature it frequently occurs in the form of hexagonal prisms. It has a specific gravity of 2.6, is so hard as to scratch glass and is fusible only by means of the oxyhydrogen blowpipe. It is insoluble in water and all acids with the exception of hydrofluoric acid with which it forms silicon fluoride and water. It is, however, soluble in the solutions of the fixed alkalies.

When a portion of the sodium hydroxide solution of silica, commonly known as sodium silicate, or water glass, is treated with a few drops of hydrochloric acid, gelatinous silicic acid will separate out. If, however, a portion is quickly poured into an excess of dilute hydrochloric acid, the silicic acid will remain dissolved in the water, together with the sodium chloride formed. The sodium chloride can be separated from the silicic acid only by dialysis.

12. Natural crystallized silica is not soluble in boiling solutions of the alkalies nor is it soluble in any of the acids with the exception of hydrofluoric acid. The amorphous variety,

on the other hand, is readily soluble in boiling alkalies. Thus, silica is found to exist in two modifications and is dimorphous. A crystal of quartz may be heated to a bright redness without change; but if powdered previous to being heated its specific gravity changes from 2.6 to 2.4, and it becomes soluble in boiling alkalies. In other words, by fine grinding and heating the crystalline modification becomes converted into the amorphous.

By far the greatest number of minerals are silicates. Clays are aluminum silicates, meerschaum and talc are silicates of magnesium, feldspar is a silicate of aluminum and potassium, the various glasses are silicates of sodium, potassium, lead, calcium, etc. The majority of the silicates are represented as derivatives of metasilicic acid and polysilicic acids of the general formula $nH_2O \cdot SiO_2$.

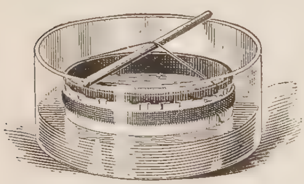


FIG. 1

13. Dialysis.—By dialysis (from the Greek, meaning *to rend asunder*) is meant the separation of dissolved substances from one another by taking advantage of the different rates at which they pass through moist diaphragms. Substances which crystallize (crystalloids) and mineral acids pass through diaphragms much more rapidly than do amorphous substances (colloids).

Thus, if a solution containing sodium chloride and silicic acid is poured upon a dialyzer the sodium chloride will pass through the membrane rapidly while the silicic acid goes through very slowly and in this manner a very complete separation may be effected. The form of dialyzer generally used in laboratories is illustrated in Fig. 1. It consists of parchment paper stretched over a hard rubber ring and held in position by a concentric ring. When the apparatus is to be used it is suspended on the surface of water and the solution to be dialyzed is poured upon it.

14. Uses of Silica.—Silica is largely employed in all its various forms. Rock crystal is used for the manufacture of

ornaments, etc. Chalcedony, onyx, and opal are sought by the engraver and lapidary. Agate, which is very hard, is used for the manufacture of mortars, etc. Sandstone serves for building purposes and for grindstones; sand, for mortars, the manufacture of glass, pottery, etc.

Fused silica ware either transparent or opaque is now largely used in commercial laboratories in the form of crucibles, evaporating dishes, and tubes. It has a great physical advantage over porcelain ware in that it may be heated to a red heat and immersed in water if necessary without cracking it; in other words, it withstands extreme and sudden temperature changes.

SILICON TETRACHLORIDE

Formula $SiCl_4$. Molecular weight 170.14

15. Preparation and Properties.—Silicon tetrachloride is formed when silicon is heated to dull redness in a current of chlorine, or when the latter gas is passed over an incandescent mixture of charcoal and silica according to the equation

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$$

Silica, lampblack, and oil are thoroughly mixed into a stiff paste which is made into little balls that are placed in a crucible the cover of which is then luted, and the whole is heated to redness in a furnace. When cool the balls are introduced into a porcelain tube or a clay retort which is heated to bright redness in a furnace while a current of carefully dried chlorine is passed through. The silicon tetrachloride and the carbon monoxide formed are passed through two **U** tubes surrounded by a freezing mixture by which the silicon tetrachloride is condensed.

Silicon tetrachloride is a colorless, heavy liquid, specific gravity 1.52, and is volatile. Its boiling point is 59° C. and it fumes readily when exposed to air, the moisture of which decomposes it, yielding hydrochloric acid and orthosilicic acid according to the equation

$$SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl$$

Because of its fuming qualities it was used during the World War for the purpose of developing smoke screens by which our battleships and transports were to a certain extent protected from German submarines.

16. Silicon Hexachloride.—Silicon hexachloride, Si_2Cl_6, is formed when silicon tetrachloride is passed over silicon heated to whiteness in a porcelain tube. It is a colorless liquid, specific gravity 1.58, that solidifies at $-1°$ C. and boils at 146° C. It fumes strongly in the air and takes fire when heated.

SILICON, IODINE, AND BROMINE

17. With bromine and iodine, silicon forms also the compounds $SiBr_4$, Si_2Br_6, SiI_4, and Si_2I_6, which are analogous in composition to the chlorine compounds. Silicon tetrabromide, $SiBr_4$, is a colorless, heavy liquid that boils at 153° C. and solidifies to a crystalline mass melting at 5° C. Silicon hexabromide, Si_2Br_6, forms large crystalline tablets, melts when heated, and distils without decomposition at 265° C. Silicon tetraiodide, SiI_4, is obtained by direct combination; it melts at 120.5° C. and boils at 290° C.; it takes fire when heated in the air and burns with a reddish flame; it is decomposed by water into hydriodic and silicic acids. Silicon hexiodide, Si_2I_6, is obtained when silicon tetraiodide is heated at 280° C. with finely divided silver. It crystallizes from carbon disulphide in beautiful, colorless, hexagonal prisms or rhombohedrons, which, on exposure to moist air, are converted into a white mass, with the formation of silicic and hydriodic acids. Subjected to heat, silicon hexiodide decomposes. Ice-cold water also decomposes it, with the formation of a white substance, $H_2Si_2O_4$, known as a disilicic acid. This compound is decomposed by weak bases into hydrogen and silica.

SILICON TETRAFLUORIDE

Formula SiF_4. Molecular weight 104.3

18. Silicon tetrafluoride is formed when hydrofluoric acid acts on silica, thus:

$$SiO_2+4HF=SiF_4+2H_2O$$

It is ordinarily prepared by heating a mixture of powdered glass or white sand and fluorspar with concentrated sulphuric acid. It may be formed also by a direct union of the elements. The reaction showing the formation of silicon tetrafluoride from fluorspar, sand, and sulphuric acid is:

$$2CaF_2+SiO_2+2H_2SO_4=2CaSO_4+SiF_4+2H_2O$$

Silicon tetrafluoride is a colorless, fuming, pungent gas that condenses to a colorless liquid under a pressure of 30 atmospheres and solidifies at −97° C. It melts at −77° C., forming a transparent mobile liquid which boils at −65° C. at 22.5 millimeters pressure. The gas resembles hydrofluoric acid in appearance; but if a moistened glass rod is exposed to the gas the wet surface quickly becomes coated with a white film of silica. This crust is formed by the decomposition of the tetrafluoride by the water on the rod, thus:

$$3SiF_4+4H_2O=2H_2SiF_6+Si(OH)_4$$

19. Fluosilicic Acid.—Fluosilicic acid, H_2SiF_6, is formed by passing silicon tetrafluoride into water, as already stated. As the silicic acid separates in a gelatinous mass that would stop the opening of the gas delivery tube, the tube is made to dip into a little mercury underneath the water. To obtain the fluosilicic acid, the thick jelly is pressed through a linen filter and the filtrate is concentrated at a low temperature. The saturated solution is a strongly acid, fuming liquid which on boiling decomposes into silicon tetrafluoride and hydrofluoric acid.

SILICON AND SULPHUR

20. Silicon Disulphide.—Silicon disulphide, SiS_2, is formed when the vapor of carbon disulphide is passed over a white-hot mixture of silica and carbon. It crystallizes in long,

white, silky needles that are decomposed into hydrogen sulphide and silica by water, and which burn in the air to silica and sulphur dioxide.

SILICON AND NITROGEN

21. A compound of silicon and nitrogen, silicon nitride, SiN, is obtained when silicon is heated to a high temperature in an atmosphere of nitrogen, and the products are treated successively with hydrofluoric acid and potassium hydroxide. It is a green infusible powder which at a red heat is decomposed by potassium hydroxide, yielding potassium silicate, hydrogen, and ammonia.

SILICON AND CARBON

22. Silicon Carbide.—Silicon carbide, SiC, or carborundum, is prepared by heating a mixture of sand, coke, and salt in an electric furnace, carbon electrodes being used. It may be obtained pure by fusing the requisite amounts of carbon and silicon in an electric furnace. The pure carbide forms colorless or blue transparent, tabular crystals whose specific gravity is 3.12. It is nearly as hard as the diamond, is not oxidized by oxygen at 1,000° C., and is not attacked by sulphur, fused potassium nitrate, nor any acids. Melted caustic alkalies, however, decompose it.

GERMANIUM

Symbol Ge. Atomic weight 72.5

23. In 1886 Winkler discovered in the mineral argyrodite, which is a rare silver ore found near Freiberg, in Saxony, the element germanium. It is prepared by the reduction of the dioxide with hydrogen, carbon, or magnesium. It is a grayish-white, lustrous, crystalline metal, with a melting point of 916° C., and a specific gravity of 5.47. It combines directly with chlorine, oxygen, and sulphur when heated with them, is stable in the air, and volatilizes at about 1,400° C. It forms two oxides, the lower oxide, GeO, of a dark color, the hydroxide of which is obtained by precipitating the dichloride, $GeCl_2$,

with potassium hydroxide; and the higher oxide, GeO_2, by heating the metal in oxygen or with nitric acid. Its sulphides correspond with the oxides, having the formulas GeS and GeS_2, respectively. The latter forms sulphosalts or thio salts by solution in alkaline hydrosulphides,

$$GeS_2+2KHS=K_2GeS_3+H_2S$$

24. Germanium Tetrachloride.—Germanium tetrachloride, $GeCl_4$, is the most stable and most important of the compounds of germanium and chlorine. It is obtained by the direct action of chlorine on the metal. It is a colorless, fuming liquid, and boils at 86° C.

The dichloride, $GeCl_2$, is formed by heating the metal in hydrochloric-acid gas; it is a powerful bleaching and reducing agent, and by the action of water it yields an oxychloride, $GeOCl_2$.

TIN

Symbol Sn. Atomic weight 118.7

25. History and Occurrence.—Tin has been known for many thousands of years; it is spoken of by Moses (Numbers, xxxi, 22), and Homer mentions it in his Iliad. Much of the brass of the ancients was an alloy of copper and tin; and as the latter was obtained from Cornwall, England, Herodotus speaks of the British Isles as the tin islands. The principal ore of tin is stannic oxide, known as the mineral cassiterite, or tinstone; it occurs in veins running through rocks, and also in the beds of streams from the disintegration of these rocks. It is found principally in Cornwall, England, and Banca and Malacca, and also, though less abundantly, in New Hampshire and in California.

26. Preparation.—In the process adopted at the Cornish plants the tinstone is stamped to crush it and is then freed from gangue by washing. The extremely hard tinstone is not reduced to so fine a powder as the other minerals mixed with it, and the high specific gravity of the stannic oxide, which is 6.5, as against that of sand or quartz, which is 2.7, makes

the separation by water easy and complete. After being washed, the ore is roasted in a revolving or reverberatory furnace to drive off any arsenic or sulphur that may remain in the ore. The ore is again washed after the roasting to remove the ferric oxide. The purified tin oxide, which contains between 60 and 70 per cent. of tin, is intimately mixed with about one-fifth of its weight of anthracite coal and a small quantity of lime or fluorspar to form a fusible slag with the silicious impurities, and reduced in a reverberatory furnace. The impure tin obtained is cast into molds and refined by the process known as liquation.

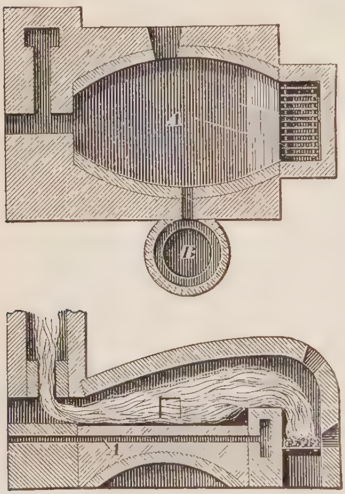


Fig. 2

The furnace used for the smelting of the tin ore is shown in Fig. 2. The mixture of tin ore and coal after being moistened to prevent the finely divided ore from being blown out of the chimney by the draft, is spread on the hearth *A*. The temperature of the furnace is gradually raised during the first 5 or 6 hours, the charge being stirred repeatedly. When the reduction is complete at the end of about 6 hours the mass is again stirred and the reduced metal allowed to run off into the iron pan *B*.

The slags drawn off from the furnace are carefully sorted, those containing much tin oxide being recharged with the next batch of ore, while those containing globules of metallic tin are crushed so that the metal may be separated by washing.

27. The impure tin obtained is purified by placing the ingots in a reverberatory furnace and gradually raising the temperature to the fusing point of tin. The pure tin, being more easily fusible, melts and flows into an cast-iron basin, while the less fusible portion, an alloy of tin, iron, arsenic, and

usually copper, remains as dross on the hearth of the furnace. The metal in the cast-iron basin is kept in a molten condition, and is stirred, or poled, with a pole of green wood. This operation may last several hours, depending on the grade of tin desired. The dross separating during this operation and the residue, or hardhead, remaining on the hearth are afterwards recharged into the smelting furnace.

The purified tin is ladled into ingots and is known commercially as block tin. Grain tin is prepared by heating block tin until the metal becomes crystalline when, owing to its brittle nature, it is broken up with hammers or allowed to fall from a height.

The purest of commercial tins is that imported from Banca, known as Banca tin or Straits tin. Next in purity is the English tin.

28. Properties.—Tin is a brilliant-white metal that does not tarnish in the air and has a specific gravity of 7.29. It is dimorphous, crystallizing in forms belonging to the quadratic and isometric systems. It is quite malleable and may be beaten into very thin leaves; at 100° C. it is ductile and can be drawn into wire. Its tenacity is small. It crackles when a bar of it is bent, producing that peculiar noise known as the *cry of tin*. It possesses a peculiar odor and is a good conductor of heat and electricity. Its melting point is about 232° C., and it distils at a white heat. Heated in air it burns readily to oxide, though it retains its luster in air at ordinary temperature. It is readily attacked by acids and dissolves in aqueous solutions of the alkalies.

29. Uses.—Tin is largely used in the arts for making tinfoil, for plating iron in the manufacture of tin plate, and also as a constituent of many important and valuable alloys. With copper it forms gun metal, speculum metal, bell metal, and bronze; with lead it forms solder and pewter. Britannia metal is an alloy of tin, antimony, and copper; and with mercury, tin yields an amalgam that is used for producing the bright reflecting surface on glass mirrors.

COMPOUNDS OF TIN

30. Stannic Chloride.—Stannic chloride, $SnCl_4$, known to the alchemists in the middle ages as liquor fumans Libavii, may be obtained by the direct action of chlorine gas on tin. It is a colorless, fuming, caustic liquid that boils at 114° C. It readily unites with water, evolving heat and forming several crystalline hydrates. With alkali chlorides it forms definite compounds, the potassium salt being K_2SnCl_6. It is used in dyeing.

31. Stannous Chloride.—Stannous chloride, $SnCl_2$, is prepared by dissolving tin in hydrochloric acid. If the solution is made strong enough, some of the salt will crystallize out with 2 molecules of water, $SnCl_2.2H_2O$. This salt is largely used in dyeing and is known in commerce as tin salt. Stannous-chloride crystals dissolve readily in water. If there is but little water present the solution is perfectly clear, but if much water is added the solution becomes turbid, owing to the formation of the basic chloride, $Sn(OH)Cl$. The atmospheric oxygen dissolved in water also takes part in this decomposition of stannous chloride from which it removes part of the metal, a corresponding quantity of stannic chloride being formed.

Stannous chloride reduces many oxygenized and chlorinated compounds, and is largely used in the laboratory. It decomposes the salts of silver and mercury, setting the metal free. It decolorizes the purple solution of potassium permanganate instantly.

32. Stannic Oxide.—Stannic oxide, SnO_2, is found in nature as the mineral cassiterite, or tinstone, in the form of beautiful, hard, transparent crystals of a yellowish-brown color. It may be prepared by burning the metal in air. It is obtained as a white powder of specific gravity 6.6, that is insoluble in all acids except hydrofluoric. Owing to its hardness, it is used for polishing glass under the name of putty powder. When fused with alkali hydroxides it forms stannates.

33. Stannic Acids.—Very little that may be regarded as accurate is known concerning the composition of the stannic acids.

When air is allowed to act on a boiling, aqueous solution of stannous chloride, a precipitate of stannic hydroxide is formed; thus:

$$2SnCl_2+6H_2O+O_2=2Sn(OH)_4+4HCl$$

On drying, the precipitated stannic hydroxide loses water, leaving a compound having the empirical formula H_2SnO_3, which is known as stannic acid.

34. Sodium and Potassium Stannates.—Of the salts of stannic acid, that of sodium, Na_2SnO_3, is probably the most important. It is prepared by fusing stannic oxide with caustic soda. The melt is then dissolved in water and the sodium stannate allowed to crystallize. It is extensively used in calico printing and dyeing. Potassium stannate is prepared by fusing stannic oxide with caustic potash.

35. Metastannic Acid.—Metastannic acid, $H_{10}Sn_5O_{15}$, is formed as a white powder when concentrated nitric acid reacts with tin; thus:

$$15Sn+20HNO_3+5H_2O=3H_{10}Sn_5O_{15}+20NO$$

Metastannic acid may be distinguished from stannic acid as follows: (1) It is insoluble in nitric acid, while stannic acid dissolves readily. (2) It is insoluble in sulphuric acid and forms a gelantinous mass. Stannic acid is soluble and does not gelatinize. (3) Metastannic acid unites with hydrochloric acid to form a compound which is not acted upon by acids but which is soluble in water. Stannic acid dissolves readily in hydrochloric acid.

The salts of metastannic acid may be prepared by the action of the alkalies upon the acid.

36. Stannous Oxide.—Stannous oxide, SnO, is of little practical importance. It is obtained by heating stannous oxalate in a closed vessel, and is a black, crystalline powder that is combustible in air. If water is added to SnO, a hydrate is formed that gradually absorbs oxygen from the air and

passes into stannic acid. With sulphuric acid it forms stannous sulphate, $SnSO_4$.

37. Sulphides of Tin.—Stannous sulphide, SnS, is obtained by leading hydrogen sulphide through a stannous solution. It is a dark-brown or black precipitate that dissolves in polysulphides of the alkalies with the formation of alkali sulphostannates.

Stannic sulphide, SnS_2, may be obtained either in the amorphous or crystalline form. By leading hydrogen sulphide through a solution of stannic chloride, stannic sulphide is obtained as a yellow amorphous precipitate. By heating a mixture of tin filings, sulphur, and ammonium chloride, stannic sulphide is obtained as a golden-yellow crystalline powder, known as mosaic gold, which consists of a mixture of stannic sulphide and ammonium-stannic chloride. The equations representing the reactions which take place in the preparation of mosaic gold are written as follows:

$$(1) \qquad Sn+4NH_4Cl=(NH_4Cl)_2{\cdot}SnCl_2+H_2+2NH_3$$

$$(2) \qquad 2(NH_4Cl)_2{\cdot}SnCl_2+2S=SnS_2+(NH_4Cl)_2{\cdot}SnCl_4 +2NH_4Cl$$

Mosaic gold is used as a pigment, especially for bronzing.

LEAD

Symbol Pb. Atomic weight 207.2

38. History and Occurrence.—Lead is one of those metals that have been known from the earliest ages of history; it is frequently mentioned in the Old Testament and other sacred writings. The Romans worked the lead ores of Spain and of England, and the Carthaginians those of Spain, the extent of their mining and smelting operations exciting surprise, even at the present day. The principal workable ore of lead is its sulphide, galenite, or more popularly known as galena, though it occurs also somewhat abundantly as carbonate, or cerussite; as sulphate, or anglesite; as chloroarsenate, or mimetite; as chlorophosphate, or pyromorphite; and in sundry other forms.

39. Preparation.—As the preparation of lead is a comparatively simple metallurgical process, only the methods employed in its extraction from galena, which may be considered as the chief source of this metal, will be treated. For the richer ores the first part of the process is carried on in a reverberatory furnace at a moderate temperature, whereby part of the galena is converted into oxide and sulphate:

$$2PbS+3O_2=2PbO+2SO_2$$
$$PbS+2O_2=PbSO_4$$

The temperature is then raised and the remaining sulphide reacts by double decomposition with the oxide and sulphate formed in the first stage:

$$PbS+2PbO=3Pb+SO_2$$
$$PbS+PbSO_4=2Pb+2SO_2$$

With the exception of about 10 per cent., which remains in the slags, the lead is thus obtained in the metallic condition. After running off the lead the residue in the slags is extracted by adding lime and a little coal and subjecting the mixture to further heating. The poorer ores are usually treated in a small blast furnace or cupola; this method may be employed for the working of slags. In this case iron or ferrous silicate is the active agent in the removal of sulphur, and the lead obtained contains considerable quantities of silver, copper, antimony, and other metals. Such a process is in use at Clausthal and Freiberg in Germany, and in the United States.

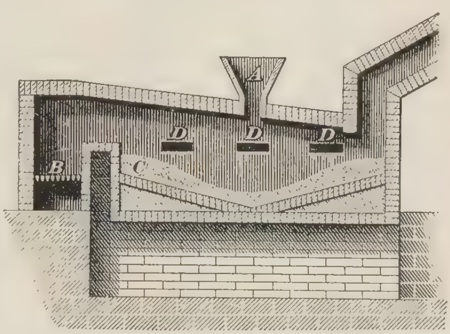


FIG. 3

40. For working the richer ores, a reverberatory furnace, Fig. 3, is employed. The essential elements in the construction of such a furnace are: The hopper A, at which the charge is

introduced; the fireplace B, at one end and separated from the hearth by a rather high fire-bridge; the hearth C, formed by molding slag in the form shown, the depression serving for collection of the molten lead, and the slopes of the hearth for spreading the charge so as to expose it to the action of the fire-gases and for working the slags; the doors D for regulating the supply of air and working the charge.

The first part of the process is carried out at dull red heat, and is essentially one of calcination and oxidation, during which the first two reactions take place. The doors are then closed and the temperature raised to a full red heat, when the last two reactions are effected.

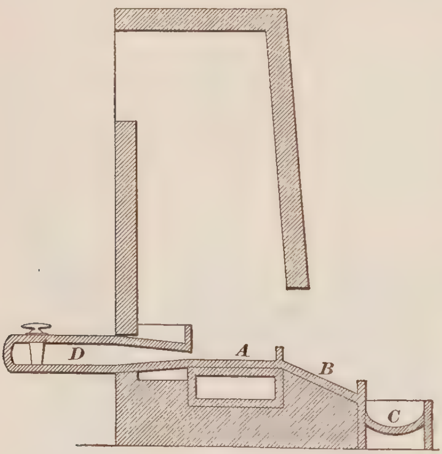


FIG. 4

41. Another form of furnace, known as the Scotch hearth, largely used in the northern parts of England, differs essentially from the foregoing in that the hearth is shallow and a blast is provided. The success of the process depends on the proper admixture of the fresh ore with that which has undergone oxidation, and in the regulation of the supply of air and fuel. The changes consist partly in those described previously, that is, the oxidation of part of the ore and the double decomposition that takes place between this and the fresh ore, and partly in reduction by the fuel added.

Fig. 4 shows in section this form of hearth; its essential parts are: The hearth A, about 4 to 6 inches deep; the work stone B, provided with shallow rim and a diagonal groove for running off the lead; the pot C, for the reception of the metal; the tuyère D, at the back of the hearth, for providing the blast. Slags are usually worked up separately in a furnace of a simi-

lar type, but having a shaft, some 3 feet high, above the hearth in which the slag and fuel are placed as in a blast furnace.

42. The lead obtained by any of these processes frequently contains sufficient antimony, besides tin, copper, iron, silver, etc., to render it hard, in which case it is put through a process of softening. The metal is heated on the bed of a reverberatory furnace until the antimony, copper, etc. become oxidized and form a scum on the surface. This is skimmed off with litharge that collects with it and the process is continued until the lead shows the proper degree of softness.

43. The method most generally adopted at the present time is to reduce the lead in blast furnaces. This method is suitable for ores containing lower percentages of lead than is necessary for the other process and also for other ores containing gold and silver as well. Ores containing considerable sulphur are roasted and mixed with silicious and basic ores containing gold, silver, and small amounts of lead, copper, arsenic, antimony, iron, and bismuth. This mixture of ores is then charged into the blast furnace together with coke and limestone. The slag from a blast furnace usually contains from 30 to 40 per cent. silica, 30 to 40 per cent. iron, and 15 to 25 per cent. lime. The sulphur remaining in the ore unites with the iron and copper to form a *matte,* or artificial sulphides of these metals, and the gold, silver, and lead are collected together. The matte is recharged with fresh ore. From time to time the lead, silver, and gold are tapped into pots and transferred to a drossing kettle.

In the drossing kettle the molten metal is allowed to cool until it begins to harden on the edges, and when this point is reached the copper, arsenic, antimony, iron, and bismuth, which have come to the surface, are skimmed off. After having been thoroughly drossed the temperature of the kettle is raised, the metal, or base bullion, is run in pigs and sent to the refinery where the gold and silver are separated from the lead.

44. Desilverizing Lead.—Among the many processes devised for the purpose of desilverizing the lead the best known are the Pattinson, Rozan, and Parkes.

The Pattinson process depends on the fact that pure lead solidifies at a somewhat higher temperature than an alloy of silver and lead. By melting the lead and then allowing it to cool, the purer lead crystallizes out first; if this is removed by a perforated ladle, the remaining liquid is richer in silver. By repeating this treatment the silver accumulates until a ton of the lead contains as much as 600 to 700 ounces of silver, after which the silver is best separated by cupellation.

The Rozan process is similar in principle, but the proper temperature is attained by the use of high-pressure steam and reduced by water. Much larger quantities can be acted on at the same time; there is the further advantage that the extreme agitation and contact with air promotes the removal of antimony and other impurities at the same time.

In the Parkes process zinc is added to the metal in suitable proportions, an alloy of lead, zinc, and silver in this case solidifying, while the lead free from silver remains molten.

45. Properties.—Lead is a soft, brilliant, bluish-white metal that leaves on paper a bluish-gray streak. It is very malleable and slightly ductile and tarnishes in the air. It has a specific gravity of 11.37, crystallizes in regular octahedrons, fuses at 327° C., and volatilizes at a bright-red heat. At a white heat it may be distilled. It has but a feeble tenacity, a wire 2 millimeters in diameter sustaining only a weight of 9 kilograms. Its freshly cut surface remains bright in perfectly dry air and also in water free from air. Lead is readily acted upon by rain water or soft waters, lead hydroxide, $Pb(OH)_2$, being formed. In contact with hard waters the lead becomes covered with a coating of basic lead carbonate, which prevents further action. Lead pipes, therefore, should not be used with soft water, but may be used with water which is slightly hard.

46. When melted in the air, lead is rapidly converted into the oxide. It is attacked slightly by sulphuric or hydrochloric acid at ordinary temperature, but dissolves readily in nitric acid. In presence of air and moisture it is acted on by feeble acids, such as acetic and carbonic acids; hence the use of vessels made of lead or soldered with lead should be avoided for cook-

ing vegetables, fruit, etc., which contain more or less acid. When taken into the system, lead unites definitely with certain tissues and is retained there, until finally sufficient to produce poisoning accumulates. Acute colic is characteristic of poisoning by a large dose of lead, but in chronic poisoning, which is far more common, there is paralysis particularly in the muscles of the forearm, causing the wrist to drop; or there may be simply an indefinable feeling of malaise, accompanied by dyspeptic symptoms.

47. Uses of Lead.—Lead is used largely in the manufacture of water and gas pipes, and, mixed with a small portion of arsenic, in the manufacture of shot. When reduced to sheets it is made into gutters, the covering of roofs, and lining for troughs and reservoirs. Alloyed with antimony and tin, it forms type metal; with bismuth, the soft alloy is used for permanent pencil points; with tin, it makes pewter and soft solder; and with tin, cadmium, and bismuth, a fusible metal which melts at 60° C.

COMPOUNDS OF LEAD

48. Lead Oxide.—Lead oxide, PbO, occurs in nature as the mineral massicot. It is prepared on a large scale in the arts under the name of litharge, by heating melted lead in a current of air. Its color is either pale yellow or orange yellow, according to the temperature at which it is prepared. Its specific gravity varies from 8.74 to 9.50. Acids dissolve it very readily, forming definite salts. Litharge is soluble in alkali-hydroxide solutions as well as in lime water. It is employed in the manufacture of glass, of lead acetate, and of white lead. It gives drying properties to linseed oil.

49. Lead Hydroxide.—Lead hydroxide, $Pb(OH)_2$, is known only as a colorless, sweetish liquid obtained by the action on lead of water and air, free from carbon dioxide. The precipitate produced by hydroxides of the alkalies in lead solutions is usually a compound having the composition $Pb_2O(OH)_2$.

50. Lead Peroxide.—Lead peroxide, PbO_2, is obtained as a brown powder by treating minium, or red lead, with dilute nitric acid and washing the precipitate with boiling water. Lead peroxide is insoluble in water; it is readily decomposed by heat, losing half its oxygen and being converted into lead oxide. It is an energetic oxidizing agent. When it is briskly triturated with sulphur the latter is ignited. If it is introduced into a test tube with sulphur dioxide the latter is immediately absorbed with formation of lead sulphate:

$$SO_2+PbO_2=PbSO_4$$

Digested with ammonium hydroxide, it forms lead nitrate,

(1) $$2NH_4OH+2PbO_2=2HNO_3+4H_2+2Pb$$

(2) $$Pb+2HNO_3=Pb(NO_3)_2+H_2$$

It sets iodine free from potassium iodide, and bleaches a solution of indigo. It combines directly with the oxides of potassium, sodium, calcium, and even lead, forming salts called plumbates having the general formula M_2PbO_3, in which M stands for a monovalent metal.

51. Lead Sesquioxide.—Lead sesquioxide, Pb_2O_3, is obtained as a reddish-yellow powder by mixing lead acetate and sodium hydroxide and adding sodium hypochlorite to this solution.

(1) $$Pb(C_2H_3O_2)_2+2NaOH=Pb(OH)_2+2NaC_2H_3O_2$$

(2) $$2Pb(OH)_2+NaClO=Pb_2O_3+NaCl+2H_2O$$

52. Red Lead.—Red lead, or minium, Pb_3O_4, is obtained by gently heating lead oxide in the air, causing it to take up oxygen. It is a mixture of $2PbO$ and PbO_2 but the commercial article varies somewhat in composition and its color varies slightly according to the method of preparation. It is used as a pigment and sometimes as a flux in the manufacture of glass, porcelain, etc. It is soluble in glacial acetic acid and in hydrochloric acid.

53. Lead Sulphide.—Lead sulphide, PbS, occurs as galena in nature in beautiful cubical crystals of a bluish-gray color and a metallic luster; its specific gravity is 7.25 to 7.70. It melts at red heat. When heated in contact with air it is

converted into oxide and sulphate and, by the action of an excess of sulphide on these compounds, metallic lead is produced. Hot, fuming nitric acid converts lead sulphide into sulphate. Concentrated and boiling hydrochloric acid transforms it into chloride with evolution of hydrogen sulphide. Lead sulphide is obtained as a black precipitate by leading hydrogen sulphide into a lead solution; it is prepared also by fusing lead and sulphur together.

54. Lead Chloride.—Lead chloride, $PbCl_2$, has been found in the crater of Vesuvius after an eruption and is known as cotunnite. It is precipitated from any lead solution, if sufficiently concentrated, on the addition of hydrochloric acid or a chloride. It is a heavy, white powder, soluble in 135 parts of cold or 30 parts of boiling water from which on cooling it crystallizes in lustrous needles. It melts when heated in closed vessels, and at a higher temperature sublimes. The fused lead chloride is translucent and sectile and is known as horn lead. White and yellow oxychlorides are used as pigments, variously known as mineral yellow, Turner's yellow, and Cassel yellow.

55. Lead Tetrachloride.—Lead tetrachloride, $PbCl_4$, is formed by passing chlorine into concentrated hydrochloric acid containing lead chloride, until it is saturated, and then adding ammonium chloride, when yellow crystals of $PbCl_4 \cdot 2NH_4Cl$, or $Pb(NH_4)_2Cl_6$, separate. When treated with ice-cold sulphuric acid, these crystals are decomposed into hydrochloric acid, ammonium sulphate, and lead tetrachloride, the latter separating as an oily liquid. Lead tetrachloride crystallizes at $-15°$ C., has a specific gravity of 3.18, and is decomposed into chlorine and the dichloride at ordinary temperature. At 105° C. it decomposes with explosive violence.

56. Lead Iodide.—Lead iodide, PbI_2, is obtained as a beautiful yellow precipitate when a solution of potassium iodide is added to a solution of a lead salt. This compound melts to a red-brown liquid at a high temperature. Lead iodide is soluble in 1,235 parts of cold or 194 parts of boiling water. Upon cooling a boiling, saturated solution, lead iodide is

deposited in golden-yellow scales, which have a magnificent luster.

57. Lead Nitrate.—Lead nitrate, $Pb(NO_3)_2$, is prepared by dissolving lead or its oxide or carbonate in dilute nitric acid, from which it crystallizes in white, regular octahedrons. The crystals dissolve in 7½ times their weight of cold water, and in a much less quantity of boiling water. At a red heat this salt is decomposed into nitrogen peroxide, oxygen, and lead oxide. It has an astringent taste and decrepitates when heated. It is used in the manufacture of matches, in dyeing, and for the preparation of other lead salts.

58. Lead Sulphate.—Lead sulphate, $PbSO_4$, occurs in nature in rather small amounts. It is obtained as a heavy white precipitate by adding sulphuric acid or a soluble sulphate to a solution of a lead salt. It is practically insoluble in water, but dissolves slightly in strong sulphuric acid; nitric and hydrochloric acids dissolve it somewhat more freely. It dissolves readily in solutions of ammonium salts, such as the tartrate and acetate. It melts at a red heat without undergoing decomposition. It is used in the preparation of rapidly drying oil varnishes and frequently as a pigment in place of white lead.

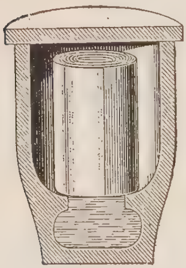


Fig. 5

59. Lead Carbonate.—Lead carbonate, $PbCO_3$, or basic carbonates of variable composition are precipitated when sodium carbonate is added to a solution of lead nitrate. The basic carbonate known as white lead is of great importance as a white pigment. If a solution of lead acetate is boiled with lead oxide and then filtered, a basic acetate is obtained, and on passing carbon dioxide through the solution a white precipitate of this basic carbonate, $2PbCO_3 \cdot Pb(OH)_2$, is deposited. Prepared in this way, however, the pigment is denser and does not possess the same covering power as that formed more gradually by the so-called Dutch process. In this process coils of sheet lead are placed in conical earthenware vessels, the lead resting on ledges, as shown in Fig. 5. The bottom of the

vessel contains weak acetic acid. These vessels, which are about 8 inches high, are stacked in layers, which are covered with tan bark or other fermenting vegetable matter; these stacks are about 15 feet square and 20 feet high. The heat generated by the fermentation gradually volatilizes the acetic acid and brings it into contact with the lead, and at the same time the carbon dioxide formed during the fermentation reacts with the basic acetate, yielding the basic lead carbonate. The acetic acid is then free to act on a further portion of lead, and the process repeats itself until practically the whole of the lead is transformed into white lead.

60. Lead Chromate.—Lead chromate, $PbCrO_4$, is found crystallized in nature, constituting the mineral crocoite. It is obtained as a yellow precipitate by adding potassium chromate to the solution of a lead salt. Lead chromate gives up oxygen readily when heated in the presence of oxidizable substances. It dissolves quite readily in solutions of alkali hydroxides. It is used as a pigment under the name of chrome yellow, and is sometimes employed as an oxidizing agent in the analysis of organic substances.

TITANIUM GROUP

TITANIUM

Symbol Ti. Atomic weight 48.1

61. Occurrence and Preparation.—Titanium exists in rutile, brookite, and anatase, which constitute three varieties of titanium dioxide, TiO_2, and with iron in titaniferous iron ores. Cubical copper-colored crystals of a nitrocyanide of titanium are frequently found in the cinders of blast furnaces in which titaniferous ores have been reduced. Pure titanium has not yet been prepared. Moissan, however, succeeded in producing a product containing about 98 per cent. of metal with about 2 per cent. carbon, by fusing the oxide with carbon in the electric furnace. Prepared in this manner titanium is a gray-white metal, specific gravity 4.87 with a brilliant white

fracture. It is harder than steel, but crumbles readily. When heated in the air it burns and at 100° C. it decomposes water with evolution of hydrogen. It does not form a compound with hydrogen, but unites directly with nitrogen at high temperatures. It dissolves in hydrochloric acid forming the hexachloride, Ti_2Cl_6.

62. Titanium and Oxygen.—Titanium forms three oxides, the dioxide, TiO_2, the sesquioxide, Ti_2O_3, and the peroxide, TiO_3. Titanium dioxide, TiO_2, is one of the principal forms in which titanium occurs in nature. To obtain pure titanium dioxide from the mineral the natural oxide is fused with potassium carbonate, when potassium titanate, K_2TiO_3, is formed. When a solution of this is treated with an acid the titanium is precipitated as hydroxide, the composition of which varies from normal titanic acid, $Ti(OH)_4$ or H_4TiO_4, to dititanic acid, $H_2Ti_2O_5$; and when the hydroxide is ignited it yields titanium dioxide in the form of a white, insoluble, infusible powder.

63. Halogen Compounds of Titanium.—Titanium tetrachloride, $TiCl_4$, is obtained by the direct union of the elements, when chlorine acts on titanium at a fairly high temperature, or it may be prepared by passing chlorine over a mixture of titanium dioxide and carbon. It is formed also by passing the vapor of chloroform over heated titanium dioxide. It is a colorless liquid that forms crystalline compounds with water, has a specific gravity of 1.76, fumes strongly in the air, boils at 136.4° C., and has a penetrating acid smell. By heating with water, it is decomposed into titanium dioxide and hydrochloric acid. The compound Ti_2Cl_6 is formed by acting on titanium with hydrochloric acid, and the compound Ti_2Cl_4 has also been obtained.

Titanium tetrafluoride, TiF_4, may be prepared by adding sulphuric acid to a mixture of titanium dioxide and fluorspar, or by acting on titanium dioxide with hydrofluoric acid. When the tetrafluoride is treated with water it forms fluotitanic acid, H_2TiF_6.

64. Titanium Salts.—The hydroxides of titanium ordinarily conduct themselves as acids, but toward the stronger acids they also act as feeble bases, forming a few salts, as example of which may be mentioned titanium sulphate, $Ti(SO_4)_2$, and titanyl sulphate, $TiOSO_4$.

ZIRCONIUM

Symbol Zr. Atomic weight 90.6

65. Occurrence and Preparation.—Zirconium is a rather rare element. It occurs in nature principally as the mineral zircon, which is a silicate having the formula $ZrSiO_4$. Zirconium is obtained free by heating potassium fluozirconate to a high temperature with aluminum. The fluozirconate is thus decomposed, yielding zirconium in a crystalline condition, somewhat resembling bismuth or antimony. Zirconium dissolves in hot concentrated hydrochloric acid. Free zirconium, like carbon, is known in three modifications. It forms hard, steel-gray plates having a specific gravity of 4.1, oxidizes very slowly in the air, but burns in the oxyhydrogen flame.

66. Zirconium and Oxygen.—Zirconium dioxide may be obtained from zircon. Zirconic acid, $Zr(OH)_4$ or H_4ZrO_4, is precipitated from acid solutions of zirconium by ammonia; when this precipitate is heated it loses water and yields the dioxide, ZrO_2. Zirconium dioxide is a rather feeble acid oxide. When fused with sodium or potassium carbonate it replaces the carbon dioxide, forming the corresponding zirconate, K_2ZrO_3.

67. Halogen Compounds of Zirconium.—Zirconium tetrachloride, $ZrCl_4$, is formed by dissolving the element in hot concentrated hydrochloric acid, or by the direct union of the elements, when chlorine acts on zirconium. It is more stable than silicon or titanium tetrachloride and is only partly decomposed by the action of water, forming zirconium oxychloride, $ZrOCl_2$. This is due to the fact that zirconium acts both as an acid-forming and base-forming element.

Zirconium tetrafluoride is obtained by passing hydrochloric-acid gas over a mixture of finely powdered zircon and fluorspar at a high temperature. It unites with fluorides of the metals, forming fluozirconates, which are analogous to fluosilicates and fluotitanates.

CERIUM

Symbol Ce. Atomic weight 140.25

68. Occurrence and Preparation.—Cerium occurs in the mineral cerite and is obtained by the electrolysis of the chloride. It is prepared also by heating the dioxide with powdered magnesium. It is a gray, ductile, malleable metal that does not change in dry air, but tarnishes in moist air. It melts at 623° C., has a specific gravity of from 6.6 to 7, ignites in the air more readily than does magnesium, and burns with extreme brilliancy. When scratched or rubbed with metal, the finely divided particles of cerium take fire. Alloyed with iron, it is used as an igniter for inflammable vapors in safety lamps. It dissolves in dilute acids, and slowly decomposes water.

69. Cerium and Oxygen.—Cerium forms three oxides, namely, the dioxide, CeO_2, the sesquioxide, Ce_2O_3, and the peroxide, CeO_3. The first two are basic in character and form salts known as the ceric and cerous. The cerous salts are mostly colorless, while the ceric are yellow or brown.

70. Halogen Compounds of Cerium.—Thus far the only chloride of cerium that has been obtained is the cerous chloride having the formula $CeCl_3$. The tetrafluoride, CeF_4, is obtained, however, by treating the hydroxide $Ce(OH)_4$ with hydrofluoric acid.

THORIUM

Symbol Th. Atomic weight 232.15

71. Occurrence and Preparation.—Thorium was discovered by Berzelius in 1828, in the mineral thorite found in Norway, which is essentially a silicate of thorium, having the formula $ThSiO_4$. By treating the tetrachloride $ThCl_4$ with

silicon or potassium, it is obtained free in the form of a dark-gray powder. When strongly heated in the air it ignites, burning with a bright flame, and forms thorium dioxide, ThO_2. It has a specific gravity of 11.0, is difficultly soluble in hydrochloric acid, but is readily soluble in nitric acid and aqua regia. It is radio active.

72. Thorium and Oxygen.—Thorium dioxide, frequently called thoria, is formed when thorium burns in air. It is a pure white powder, almost entirely infusible, and is incandescent in high temperatures, giving a brilliant light. For this reason it is largely used, in connection with a few other rare oxides, for the manufacture of the mantles used in the Welsbach light. Unlike the other members of the group, thorium dioxide does not form thorates, but acts as a base, forming salts in which thorium acts as a quadrivalent element.

73. Halogen Compounds of Thorium.—Thorium tetrachloride, $ThCl_4$, is obtained by heating an intimate mixture of the dioxide and carbon in dry chlorine. It is not decomposed by water at ordinary temperature, but if its solution in water is evaporated, hydrochloric acid is evolved and thorium dioxide remains. With potassium chloride, the tetrachloride forms potassium chlorthorate, K_2ThCl_6.

Thorium tetrafluoride, ThF_4, is obtained as a white powder by treating the tetrachloride with hydrofluoric acid. It unites with potassium fluoride, forming potassium fluothorate, K_2ThF_6.

CHROMIUM GROUP

74. Introductory.—The chromium group consists of the elements chromium, molybdenum, tungsten, and uranium, which form the oxides CrO_3, MoO_3, WO_3, and UO_3, and the acids H_2CrO_4, H_2MoO_4, H_2WO_4, and H_2UO_4. In these compounds they closely resemble the members of the oxygen-sulphur group, but when they lose oxygen they form compounds that have little or no acid character. As the lower oxides of chromium are basic, there are a large number of salts in which chromium acts as a base. Molybdenum and

tungsten do not appear to possess basic properties and form very few salts. Uranium acts in a rather peculiar manner; it enters into compounds combined with 2 atoms of oxygen, as the compound UO_2, which acts like a bivalent metal, forming uranyl salts; thus the sulphate is UO_2SO_4. These salts appear to be derived from a base $UO_2(OH)_2$, but this compound also has distinct acid properties. On the basis of practical usage in the industries, chromium is the most important member of this group, and will be treated first.

CHROMIUM

Symbol Cr. Atomic weight 52.0

75. History and Occurrence.—Chromium was discovered in 1797 by Vauquelin in a mineral obtained from Siberia, known as crocoite, which is a chromate of lead, $PbCrO_4$. It derives its name from a Greek word meaning color, in allusion to the varied colors of its compounds, on which their uses in the industries largely depend. It occurs in nature chiefly as the mineral chromite, $Fe(CrO_2)_2$, or chrome iron, a combination of chromium oxide and ferrous oxide, probably a ferrous salt of metachromous acid, $HOCrO$.

76. Preparation and Properties.—Chromium may be obtained by mixing chromic oxide with powdered aluminum and igniting the mixture, the following reaction taking place:

$$Cr_2O_3+2Al=Al_2O_3+2Cr$$

Chromium is a light-gray, or tin-white, lustrous, crystalline substance. It is very hard and difficult to fuse, and oxidizes very slowly when heated in the air, but heated in oxygen or in the oxyhydrogen flame, it burns to chromic oxide, Cr_2O_3. It is insoluble in nitric acid, but dissolves in hydrochloric and hot sulphuric acids. Its specific gravity is 6.81, and its melting point is 1,520° C. It is non-magnetic. Large quantities are used in the form of an alloy, ferrochrome, containing between 60 and 70 per cent. of chromium. These ferrochromes are used to introduce chromium into steel, thereby greatly increasing the hardness of the steel.

COMPOUNDS OF CHROMIUM

77. Hydroxides of Chromium.—Chromous hydroxide, $Cr(OH)_2$, is obtained as a light-brown precipitate when potassium hydroxide is added to a solution of chromous chloride. It readily gives up water and hydrogen and is converted into chromic oxide, Cr_2O_3.

Chromic hydroxide, $Cr(OH)_3$, is obtained as a light-blue precipitate by adding ammonia to a solution of a chromic salt, and carefully drying in a vacuum the precipitate thus formed. When heated, this decomposes first into $CrOOH$ and finally into Cr_2O_3. Sodium and potassium hydroxides dissolve chromic hydroxide with the formation of the corresponding chromites, which are derivatives of the acid $CrOOH$. When solutions containing these chromites are boiled, chromic hydroxide is precipitated, but this precipitate always contains some of the alkali metal in combination.

78. Chromic Oxide.—Chromic oxide, or chromium sesquioxide, Cr_2O_3, may be prepared by heating either of the hydroxides, but is more readily obtained on a large scale by heating a mixture of potassium dichromate and sulphur, when potassium sulphate and chrome oxide result. Obtained in this way, it is a green powder that becomes almost insoluble in acids when heated. It is used in coloring glass and in china painting.

79. Chromium Trioxide.—Chromium trioxide, CrO_3, may be prepared by treating a concentrated solution of an alkali chromate or dichromate with concentrated sulphuric acid, when the trioxide crystallizes from the solution in fine red needles. It is deliquescent and when dissolved in water gives an acid solution which, when neutralized, yields chromates, indicating that the solution contains chromic acid, H_2CrO_4. When heated, the trioxide gives up half its oxygen and is converted into chromic oxide. It is a powerful oxidizing agent and is reduced by almost any oxidizable substance.

80. Chromous Chloride.—Chromous chloride, $CrCl_2$, may be obtained by reducing chromic chloride by hydrogen at a moderate heat. It is a white, crystalline substance, soluble in

water, forming a blue solution that, by absorption of oxygen, rapidly changes to green.

81. Chromic Chloride.—Chromic chloride, $CrCl_3$, is the most important compound of chromium and chlorine. It may be obtained by passing chlorine gas over an ignited and perfectly dry mixture of chrominum and charcoal. A sublimate of brilliant, peach-blossom-colored scales is thus obtained, which is almost insoluble in cold and only sparingly soluble in boiling water, forming with the latter a green solution.

It may be prepared in solution by dissolving chromic hydroxide in hydrochloric acid. This solution has a deep green color, and when sufficiently concentrated deposits crystals having the composition $CrCl_3{\cdot}6H_2O$. When these crystals are heated in the air, they are decomposed with the formation of chromic oxide, but if heated in an atmosphere of chlorine or hydrochloric acid the water is expelled and the reddish-violet anhydrous chloride remains. This dissolves in water, forming a green solution, but if first sublimed it becomes almost insoluble in water and acids. With the chlorides of the alkalies it forms double salts, as examples of which may be mentioned $KCrCl_4$ and K_2CrCl_5.

82. Chromium Oxychloride.—Chromium oxychloride, or chromyl chloride, CrO_2Cl_2, is obtained by heating a previously fused mixture of common salt and potassium dichromate with sulphuric acid; abundant red vapors are disengaged, and condensed to a blood-red liquid. It boils at 116.8° C. On contact with water it decomposes into hydrochloric acid and chromic acid.

83. Chromium Sulphate.—Chromium sulphate, $Cr_2(SO_4)_3$, may be prepared in solution by dissolving chromic hydroxide in sulphuric acid. If the solution is allowed to evaporate slowly, it will deposit the sulphate in purple crystals having the composition $Cr_2(SO_4)_3{\cdot}15H_2O$, but if the solution is first boiled it turns green and the sulphate will not crystallize from it. If, however, the green solution is allowed to stand for some time it becomes purple again and purple crystals of sulphate separate. It appears to be true of the solutions of

chrominum salts in general that they exist in two modifications: a purple modification from which crystals are readily obtained, and a green variety, obtained by boiling the purple form, from which crystals cannot be obtained. The green solution changes back to purple if allowed to stand for some time.

84. Chrome Alum.—Like aluminum sulphate, chrominum sulphate combines with the sulphates of the monovalent metals, forming double sulphates that crystallize from solution with 24 molecules of water. The most important of these, the double sulphate of chromium and potassium, known as chrome alum, has the formula $Cr_2(SO_4)_3K_2SO_4{\cdot}24H_2O$. It is prepared by reducing a solution of potassium dichromate containing sulphuric acid, by means of sulphur dioxide. Neglecting the water of crystallization, which is furnished by the solution, the equation representing its formation may be written:

$$K_2Cr_2O_7+H_2SO_4+3SO_2=Cr_2(SO_4)_3K_2SO_4+H_2O$$

Chrome alum is used in tanning and dyeing and to a slight extent in photography.

85. Chromic Acid and Chromates.—Chromous compounds when exposed to the air or treated with oxidizing agents are readily oxidized to chromic compounds, which is the limit of oxidation if an acid is present. In these compounds chromium acts as a base and is usually regarded as such. If, however, the oxidation is carried out in the presence of a strong base, it proceeds further and a chromate results. In these compounds chromium plays the part of an acid-forming element, and the chromates are derived from the hypothetical chromic acid, H_2CrO_4. This acid has not been obtained in the free state, as it breaks up into chromium trioxide and water when set free from its compounds. It is believed that these acids exist in aqueous solution, for when chromium trioxide is dissolved in water and the solution is neutralized by a base, a chromate is formed. The chromates in general resemble the sulphates. It has been stated that sulphuric acid loses water and forms pyrosulphuric or disulphuric acid. In the same way, theoretically, chromic acid is converted into

dichromic acid. Neither of these acids exists in the free state, but in all probability the relation between chromates and dichromates is the same as between sulphates and disulphates. By treating a chromate with an acid, a dichromate is obtained. Thus, if potassium chromate is treated with nitric acid, the following reaction takes place:

$$2K_2CrO_4+2HNO_3=K_2Cr_2O_7+2KNO_3+H_2O$$

On the other hand, if a dichromate is treated with an alkali hydroxide, a chromate results. This may be illustrated by the equation:

$$K_2Cr_2O_7+2KOH=2K_2CrO_4+H_2O$$

86. Potassium Chromate.—Potassium chromate, K_2CrO_4, is obtained by adding potassium hydroxide to the solution of the dichromate. It crystallizes in yellow rhombic crystals, is permanent in the air, has a cooling taste and an alkaline reaction. It dissolves very easily in water and is therefore difficult to purify; for this reason it is usually converted into the dichromate, which is readily purified.

87. Potassium Dichromate.—Potassium dichromate, $K_2Cr_2O_7$, is prepared from chromite. The chromite is roasted and then ground and mixed with potassium carbonate and lime, and heated. Calcium and potassium chromates are formed, and these are dissolved in water. Potassium sulphate is added to the solution, when calcium sulphate is precipitated and all the chromium is converted into potassium chromate. The solution is then treated with the proper amount of sulphuric acid, the chromate being converted into the dichromate. As it dissolves in 10 parts of water at ordinary temperature, and is much more soluble in hot water, it crystallizes, on cooling, in large red plates belonging to the triclinic system. As the dichromate crystallizes well, it is easily purified by recrystallization. The chromate and dichromate may be regarded as the starting point for the preparation of the other compounds of chromium. When heated, the dichromate fuses without decomposing, but at a higher temperature it breaks up into potassium chromate, chromic oxide, and oxygen. When heated with sulphuric acid, the potassium and chromium unite with

the acid, forming chrome alum. Water is evolved, and all the oxygen not used in the formation of these is set free.

Potassium dichromate is largely used as an oxidizing agent. It is also used in dyeing, to a certain extent in photography, and as the starting point for the preparation of nearly all the other chromium compounds.

88. Sodium Chromate.—Sodium chromate, Na_2CrO_4, is obtained just as is potassium chromate; and by treating it with an acid, sodium dichromate, $Na_2Cr_2O_7$, is obtained. These compounds closely resemble the corresponding potassium salts, and are now used extensively in place of the more expensive potassium compounds.

89. Barium Chromate.—Barium chromate, $BaCrO_4$, is obtained as a yellow precipitate when a soluble chromate is added to the solution of a barium salt. It is insoluble in water and in acetic acid, but dissolves in nitric and hydrochloric acids. It is used somewhat as a pigment under the name of lemon yellow.

90. Lead Chromate.—Lead chromate, $PbCrO_4$, occurs in nature as crocoite. It may be prepared by adding a soluble chromate or dichromate to the solution of a lead salt, when the chromate separates as a yellow precipitate that is used as a pigment under the name of chrome yellow. When treated with a small quantity of a dilute solution of a hydroxide, it turns red owing to the formation of basic lead chromate, Pb_2OCrO_4, known as chromate red. This is used in dyeing, by coloring the substance in chrome yellow and then dipping it in a bath of lime water, when the chrome yellow is changed to chrome red, and the substance is consequently dyed red.

91. Silver Chromate.—Silver chromate, Ag_2CrO_4, is formed as a brick-red precipitate when a solution of silver nitrate is treated with a solution of potassium chromate. The dichromate is obtained when potassium dichromate is added to a slightly acid solution of silver nitrate. It forms small scarlet triclinic crystals.

MOLYBDENUM

Symbol Mo. Atomic weight 96

92. Occurrence and Properties.—Molybdenum occurs principally as sulphide, or molybdenite, MoS_2, as lead molybdate, or wulfenite, $PbMoO_4$, and frequently as molybdenum ochre, MoO_3. It is prepared by reducing the oxides or chlorides of molybdenum by a current of hydrogen at a high temperature. It is a white, very hard, brittle metal, and is almost infusible. It has a specific gravity of 10.28 at 26° C., and oxidizes, when heated in the air, to molybdenum trioxide. It forms four oxides: MoO, Mo_2O_3, MoO_2, and MoO_3.

COMPOUNDS OF MOLYBDENUM

93. Oxides.—Molybdenum trioxide, MoO_3, frequently called molybdic acid, is obtained by roasting at a moderate temperature the natural molybdenite, MoS_2; the resulting oxide is dissolved in ammonia and the solution filtered. On evaporation and cooling, crystals of ammonium molybdate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, are obtained, which yield molybdenum trioxide when strongly heated in the air. Molybdenum trioxide is a white, fusible, volatile powder.

Molybdic oxide, Mo_2O_3, is formed as a black precipitate when a solution of the trioxide is treated with a reducing agent, such as sodium amalgam.

Molydenum dioxide, MoO_2, is a dark-blue compound, obtained by gently heating molydenum or molybdic oxide in air.

Molybdenum monoxide, MoO, is obtained as a black precipitate by treating a solution of molybdenum dichloride with a hot solution of potassium hydroxide.

94. Sulphides of Molybdenum.—Molybdenum disulphide, MoS_2, occurs in nature as molybdenite; it thus occurs in masses of tabular crystals that possess a strong metallic luster and steel-gray color and leave a gray streak on paper, similar to graphite. The same compound is produced artificially by heating the trisulphide or by igniting the trioxide

with sulphur. When roasted in contact with the air, it is converted into trioxide.

The trisulphide, MoS_3, is obtained by passing hydrogen sulphide into a concentrated solution of a molybdate in the presence of hydrochloric acid. It is a reddish-brown powder that is slowly dissolved by alkalies, more easily by alkaline sulphides, forming sulphur salts called thiomolybdates. The thiomolybdates of the alkaline metals, alkaline earths, and magnesium are soluble in water, forming solutions of a fine red color.

95. Chlorides of Molybdenum.—Molybdenum forms four chlorides, the formulas of which appear to be $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$.

The pentachloride, $MoCl_5$, is obtained when pure metallic molybdenum is heated for some time in a stream of chlorine. If this pentachloride is heated to about 250° C. in a stream of hydrogen it is reduced to the red trichloride, $MoCl_3$, which volatilizes with difficulty; this compound heated to redness in an atmosphere of carbon dioxide free from oxygen, is resolved according to the equation $2MoCl_3 = MoCl_2 + MoCl_4$ into the yellow dichloride, which remains in the tube, and the brown tetrachloride, which either sublimes or is carried forward by the stream of gas. Of these four chlorides the pentachloride is the only one that crystallizes distinctly, and melts and volatilizes without decomposition. The pure pentachloride is black and its vapor has a dark, brown-red color. The yellow dichloride and the red trichloride, which latter closely resembles amorphous phosphorus, have both been obtained in the amorphous state. In an atmosphere of carbon dioxide, the dichloride bears a bright-red heat without melting or volatilizing; the trichloride, under the same circumstances, is resolved into dichloride and tetrachloride, which, when again heated, splits up into pentachloride, which sublimes, and trichloride, which remains behind.

96. The dichloride and trichloride are permanent at ordinary temperatures in the atmosphere and insoluble in water; the tetra and pentachlorides, on the other hand, are rather

unstable, being very susceptible to the action of oxygen and moisture. The dichloride is insoluble in nitric acid, which readily dissolves all the other chlorides. The dichloride dissolves easily when heated with hot hydrochloric acid, and crystallizes therefrom on cooling, in long, yellow lustrous needles.

The bromides of molybdenum are similar to the chlorides in composition.

97. Molybdic Acid.—Molybdenum trioxide is slightly soluble in water and forms a solution having acid properties.

If this solution is neutralized by bases, molybdates are formed that are similar to the chromates in composition. When the ammonium salt thus obtained is treated with dilute nitric acid it is decomposed, and molybdic acid, $H_2MoO_4{\cdot}H_2O$, crystallizes out of the solution. A number of salts are derived from this acid; but as the acid has a great tendency to combine with itself, most of the salts are derived from polymolybdic acids. Molybdic acid also unites with other acids, forming complicated acids that unite with bases forming complex salts. The best known of these acids is phosphomolybdic acid, a combination of phosphoric and molybdic acids. When phosphoric acid or a soluble phosphate is added to a solution of ammonium molybdate in an excess of nitric acid, a yellow precipitate of ammonium phosphomolybdate separates; this is a salt of phosphomolybdic acid, having the formula

$$(NH_4)_3PO_4{\cdot}12MoO_3{\cdot}6H_2O$$

TUNGSTEN

Symbol W. Atomic weight 184

98. Occurrence and Preparation.—Tungsten occurs in nature in a few minerals. Its symbol, *W*, is derived from the mineral wolframite, which is tungstate of iron and manganese, and from which it was first obtained; it occurs in scheelite, which is calcium tungstate; in stolzite, which is lead tungstate; etc. Metallic tungsten is obtained by reducing tungsten trioxide, WO_3, with hydrogen or aluminum powder as an iron-gray metal of specific gravity 18.77. It is extremely hard,

melts at 3,267° C., and is unaffected by either hydrochloric or sulphuric acid, though it is converted into tungstic acid by the action of nitric acid. When dissolved in about ten times its own weight of fused steel, tungsten forms an extremely hard alloy, known as tungsten steel, that is used in the manufacture of machinists' tools. One of the most peculiar properties of tungsten is its ability to increase the magnetic power of the steel with which it is alloyed. A horsehoe magnet of ordinary steel, weighing 2 pounds, for instance, is generally considered of very good quality if it bears seven times its own weight, but a similar magnet made of an alloy of steel and tungsten is able to bear nearly twenty times its own weight.

COMPOUNDS OF TUNGSTEN

99. Oxides.—Tungsten dioxide, WO_2, appears to be a chemically indifferent oxide, and is obtained by reducing tungsten trioxide with hydrogen at a low red heat, when it forms a brown powder that is dissolved by boiling in solution of potassium hydroxide, hydrogen being evolved, and potassium tungstate formed, according to the equation

$$2KOH+WO_2=K_2WO_4+H_2$$

Tungsten trioxide, WO_3, is obtained by decomposing metallic tungstates with nitric acid, and heating the tungstic acid thus precipitated. It is a canary-yellow powder, becoming orange when heated and yellow again when cooled.

100. Chlorides.—Tungsten hexachloride, WCl_6, is obtained as a bronze-colored substance when tungsten is heated in dry chlorine. It fuses at 275° C. and boils at 346° C.

The pentachloride, WCl_5, is obtained as shining black crystals by distilling the hexachloride in a current of hydrogen or carbon dioxide. It melts at 248° C., boils at 276° C., is very hygroscopic, exposure to the air instantly covering the crystals with a golden-green film.

The tetrachloride, WCl_4, is obtained by gently igniting WCl_6, or WCl_5, in an atmosphere of hydrogen. It is a grayish-brown substance. It is very hygroscopic, although not to quite the

extent of the pentachloride and is decomposed by cold water into the dioxide and hydrochloric acid.

The dichloride, WCl_2, is obtained by strongly igniting WCl_6 in hydrogen. It is a bright, gray, non-volatile substance. Tungsten oxychlorides are also known.

101. Tungstic Acid.—When tungsten trioxide is fused with the proper amount of potassium carbonate, or solutions of these substances are mixed in the proper proportions, potassium tungstate, K_2WO_4, is formed; if a solution of this compound is treated with a strong acid, tungstic acid is precipitated. If the solution is hot, the acid has the composition H_2WO_4; but if at ordinary temperature, the precipitate has the composition $H_2WO_4 \cdot H_2O$, corresponding to molybdic acid. Like molybdic acid, tungstic acid has a tendency to unite with itself, forming polytungstic acids, and with other acids, forming complex acids. These combine with bases, forming very complicated compounds.

URANIUM

Symbol U. Atomic weight 238.2

102. Occurrence and Preparation.—The most important sources of uranium are the minerals pitchblende, or uraninite, and carnotite; deposits of the former are found in North Carolina, Cornwall, England, and German East Africa, while the latter occurs in Colorado.

The pure metal may be prepared by strongly heating a mixture of the tetrachloride, UCl_4, with metallic sodium covered with sodium and potassium chlorides. The experiment is carried out in a crucible enclosed in a second crucible containing charcoal, so as to insure the exclusion of air. It can be prepared also by heating the oxide, pitchblende, U_3O_8, in an electric furnace with about one-tenth its weight of charcoal.

103. Properties.—Uranium is a white metal, capable of taking a high polish, and somewhat softer than steel, and is malleable. Its specific gravity is 18.7. It melts at 800° C. and is permanent in the air. It combines directly with fluorine at

ordinary temperatures; with chlorine, bromine, iodine, sulphur, and oxygen at a moderate heat; and with nitrogen at a bright-red heat. It decomposes water slowly at ordinary temperatures, and very rapidly at about 100° C. With carbon at high temperatures, it forms a carbide, U_2C_3, that acts on water, forming a mixture of gaseous, liquid, and solid hydrocarbons. The metal and its salts are radioactive; all its salts are powerful poisons.

COMPOUNDS OF URANIUM

104. Oxides.—As stated, uranium occurs in nature in the form of the oxide, U_3O_8, which is also the final product of the oxidation of uranium in the air. When this oxide is treated with nitric acid, uranyl nitrate is formed, and when this is heated, uranium trioxide, UO_3, is formed. The dioxide is formed by reducing the trioxide by means of hydrogen. When either of these oxides is ignited in the air, U_3O_8 results. The tetroxide, UO_4, is obtained as a light-yellow precipitate by adding hydrogen peroxide to a uranyl salt.

105. Chlorides.—Uranium tetrachloride, UCl_4, is formed when chlorine acts on finely divided uranium, but this is usually accompanied by some pentachloride. By reducing this with hydrogen, the trichloride, UCl_3, is obtained; and by heating the tetrachloride for some time in chlorine it is partially converted into the pentachloride. The tetrachloride, UCl_4, is the most stable of the chlorides.

106. Uranous and Uranyl Salts.—The few uranous salts are derived from tetravalent uranium, 1 atom replacing 4 of the hydrogen, as shown by the sulphate, $U(SO_4)_2$. In the uranyl compounds, the group UO_2 acts like a bivalent metal. The salts formed may be illustrated by the sulphate, UO_2SO_4, and the nitrate, $UO_2(NO_3)_2$. These salts, it is evident, are derived from the hydroxide, $UO_2(OH)_2$, which acts as a base in the presence of acids.

107. Uranates.—It has just been shown that in the presence of acids, the hydroxide, $UO_2(OH)_2$, acts as a base. In

the presence of some of the stronger bases it also acts as an acid. When a uranyl salt is acted on by an alkali hydroxide, a precipitate is formed having the composition $M_2U_2O_7$, and is therefore derived from an acid, $H_2U_2O_7$, which is analogous to dichromic acid, and is known as diuranic acid. One of the most important derivatives of this acid is sodium diuranate, $Na_2U_2O_7$, a yellow powder that is manfactured in large quantities and used in coloring glass.

RADIOACTIVE ELEMENTS

108. It was discovered by Becquerel that uraninite, or pitchblende, emitted a peculiar kind of rays which move in a straight line, act on a photographic plate, and cannot be reflected or refracted. Gases become electrical conductors when these rays are passed through them. For a while it was thought that this radioactivity was due solely to the uranium present; but M. and Mme. Curie have proved that the radioactivity is largely caused by three hitherto unknown elements which they called radium, polonium, and actinium. The amounts of these elements present were very minute, and in order to separate them from the residues left after extracting the uranium, these were subjected to numerous chemical operations and the success in concentration judged by measuring the conductivity of an air layer exposed to the rays. It will be observed that for the discovery of these elements an entirely new method of testing was introduced.

109. Radium is the most thoroughly investigated of these elements, and has been obtained nearly pure as chloride. It has an atomic weight, according to Mme. Curie, of 226. It accompanies the barium chloride extracted from uraninite and is separated from it by fractional crystallization, the radium chloride being less soluble than barium chloride. About 1 gram of radium chloride was separated in this manner from 80 tons of ore. The process is simplified by recrystallizing with the bromides instead of the chlorides. It has a characteristic spectrum resembling that of the alkaline earths.

Radium compounds give light in the dark; when they are very concentrated they transform oxygen into ozone and have an odor like sodium hypochlorite. Under the influence of the rays emitted, glass assumes a brown color and potassium and sodium chlorides turn blue. Within recent years, salts of radium have come to be extensively used by the medical profession in the treatment of cancer.

Polonium is found with bismuth extracted from uraninite; its chemical properties are similar to bismuth. The sulphide is more volatile in vacuo than bismuth sulphide, which property is taken advantage of in separating it.

Our knowledge of these elements and of actinium which resembles thorium, is very limited, and at present it is not possible to assign to them any definite place in the periodic system.

INORGANIC CHEMISTRY
(PART 12)

MANGANESE, IRON, COBALT, AND NICKEL

1. Introductory.—According to the periodic classification, manganese belongs to the same family of elements as the halogens, and therefore it might be expected that the existing relationships would be very close. The contrary is true, however, and it may be said that whatever similarity exists between the halogens and manganese is found only between the compounds Mn_2O_7 and Cl_2O_7.

Manganese is the only metallic member of the family, and in physical and chemical properties its relationship to iron and chromium is fairly close.

MANGANESE

Symbol Mn. Atomic weight 54.93

2. History and Occurrence.—Manganese was discovered by Scheele and Bergman in 1774 in a mineral then known as braunstein. Owing to its being confounded with magnetic iron, this mineral had received the Latin name of this substance, *magnesia nigra,* whence the name magnesium was first assigned to the new metal. This name was afterwards changed to manganese to distinguish it from true magnesium obtained from magnesia alba. It is found chiefly as pyrolusite, MnO_2, braunite, Mn_2O_3, and rhodochrosite, $MnCO_3$. Manganese sulphide, arsenide, and silicate are also known as minerals. The metal itself has not been applied to any very useful purpose in the arts, but it forms some useful alloys.

Manganese is best prepared by reducing MnO_2 by means of aluminum powder.

$$3MnO_2+4Al=3Mn+2Al_2O_3$$

It is a grayish-white, hard, brittle metal having a specific gravity of 7.42; it is feebly magnetic, fuses at 1,260° C., and volatilizes at the temperature of the electric furnace. It will take a high polish, but oxidizes readily in the air unless it contains iron. It decomposes water at little above the ordinary temperature, is easily soluble in all dilute acids, and combines with carbon and nitrogen at high temperatures to form the carbide, Mn_3C, and the nitride, Mn_5N_2.

COMPOUNDS OF MANGANESE

3. Manganese Dioxide.—Manganese dioxide, or peroxide, MnO_2, the chief compound and most important one of manganese, occurs in nature as pyrolusite in amorphous masses, in crystalline masses, or in steel-gray, rhombic crystals. It has a metallic luster, a black streak, and is opaque and brittle. The mineral contains from 70 to 90 per cent. of manganese dioxide which has a specific gravity of 5.026. Manganese dioxide is also found in the hydrated state as wad. Pyrolusite is also known as black oxide of manganese. It is sometimes used in the manufacture of steel, the manufacture of bleaching powder, in the making of glass, and as a source of oxygen. Manganese dioxide does not combine readily with acids, although hydrochloric acid dissolves it, giving a brown solution. If this solution is heated chlorine is evolved and the pink manganese chloride is obtained. Nitric acid has almost no action on the dioxide, but strong sulphuric acid dissolves it, evolving oxygen, thus:

$$2MnO_2+2H_2SO_4=2MnSO_4+2H_2O+O_2$$

Dilute sulphuric acid in the presence of some readily oxidizable substance such as oxalic acid or ferrous sulphate, produces the same effect.

Heating with hydrogen does not reduce the oxides of manganese to metallic manganese but forms manganous oxide, MnO.

4. Manganous Oxide.—Manganous oxide, MnO, or manganese monoxide, is obtained by the preceding method or by fusing a mixture of anhydrous manganese chloride, sodium carbonate, and ammonium chloride. Manganous oxide is practically insoluble in water and may be separated from the reaction mixture by treating the latter with water and thus dissolving out the soluble matter. It forms a green powder which when heated in hydrogen crystallizes in emerald-green octahedra having an adamantine luster and a specific gravity of 5.1. It is soluble in acids, forming the manganous salts, absorbs oxygen from the air, and fuses at a white heat without loss of oxygen. It is found in nature as the mineral manganosite.

5. Manganic Oxide.—Manganic oxide, Mn_2O_3, or manganese sesquioxide, occurs as the mineral braunite in octahedral crystals. It closely resembles the dioxide, has a brownish-black color, a semi-metallic luster, and a specific gravity of 4.8. It is soluble in strong sulphuric acid, is feebly basic, and may be obtained by heating any of the oxides of manganese to redness in a current of oxygen. Added to melted glass, it imparts a purple color to it.

6. Red Oxide of Manganese.—Red oxide of manganese, Mn_3O_4, trimanganese tetroxide, is found crystallized in tetragonal pyramids as the mineral hausmannite. It is the most stable of the oxides and is formed when any of the others is heated in the air. It is a brown or reddish-brown powder having a specific gravity of 4.7, and resembles the corresponding lead oxide. It is probably a manganous manganic oxide having the formula $MnO{\cdot}Mn_2O_3$.

7. Manganese Heptoxide.—Manganese heptoxide, Mn_2O_7, also known as permanganic anhydride, is a red, oily liquid prepared by the gradual addition of strong sulphuric acid to potassium permanganate, thus:

$$2KMnO_4+2H_2SO_4=Mn_2O_7+2KHSO_4+H_2O$$

It is an extremely unstable compound, decomposing at ordinary temperatures with the evolution of oxygen, the decom-

position being also accompanied by the emission of the violet fumes of the heptoxide. It absorbs moisture from the air and is a powerful oxidizing agent, setting fire to most combustible bodies.

8. Manganous Hydroxide.—Manganous hydroxide, $Mn(OH)_2$, forms as a white precipitate when an alkali is added to a solution of a manganous salt out of contact with the air. It must be dried in a current of hydrogen, as it speedily oxidizes to Mn_2O_3 when exposed to the air. It occurs in nature as the mineral pyrochroite.

9. Manganic Hydroxide.—Manganic hydroxide, $MnO(OH)$, occurs in nature in steel-gray crystals as the mineral manganite. It gives a brown streak on unglazed porcelain and has a specific gravity of 4.3. It is formed when manganous hydroxide is allowed to stand in the air for a short time. Dilute nitric acid dissolves part of it, forming manganous nitrate, the remainder being converted into the dioxide.

10. Manganous Chloride.—Manganous chloride, $MnCl_2$, is formed by dissolving any of the oxides or hydroxides, or the carbonate of manganese in hydrochloric acid, with the aid of heat. It is obtained in large quantities as a by-product in the preparation of chlorine for use in the manufacture of bleaching powder. When a solution containing the chloride is sufficiently concentrated, the chloride separates in pink crystals having the composition $MnCl_2 \cdot 4H_2O$. When heated, these crystals fuse to an oily liquid and in moist air at this temperature are decomposed into the oxide and hydrochloric acid.

If manganic hydroxide is dissolved in cold hydrochloric acid, a brown solution is obtained that is believed to contain manganese trichloride, $MnCl_3$. Similarly if the dioxide is dissolved in cold hydrochloric acid, a brown solution is obtained that is thought to be manganese tetrachloride, $MnCl_4$. Neither of these compounds have been isolated and if allowed to stand they gradually lose chlorine and become pink when the content of chlorine is reduced to that indicated by the formula $MnCl_2$. If heat is applied, this change takes place rapidly.

11. Manganous Sulphate.—Manganous sulphate, $MnSO_4$, is prepared by dissolving manganous carbonate, $MnCO_3$, in sulphuric acid, or by heating a paste of manganese dioxide and sulphuric acid to redness and leaching with water. The properly concentrated rose-colored solution deposits, between 0° and 6° C., oblique rhombic prisms, isomorphous with green vitriol and containing 7 molecules of water. Between 7° and 20° C., manganous sulphate crystallizes with 5 molecules of water, like cupric sulphate, with which it is then isomorphous. Between 20° and 30° C., it is deposited in oblique rhombic prisms that then contain only 4 molecules of water. All of these crystals are pink-colored, and their color is deeper the more water of crystallization they contain; all are extremely soluble in water.

12. Manganous Sulphide.—Manganous sulphide, MnS, or manganese monosulphide, occurs in nature as the mineral alabandite, in steel-gray crystalline masses having a green streak. It is prepared by heating one of the oxides of manganese, or manganese carbonate in a current of hydrogen sulphide. It is obtained in this way as a dark powder, but when heated to a high temperature it melts and forms a steel-gray crystalline mass. Alkaline sulphides precipitate manganous sulphide from solutions of manganous salts as a flesh-colored precipitate that turns brown on exposure to the air. When the flesh-colored precipitate is boiled with an excess of an alkaline sulphide it changes into a green crystalline mass. Manganous sulphide unites with the alkaline sulphides, forming salts, and is soluble in hydrochloric acid.

The disulphide, MnS_2, occurs as hauerite, has a metallic luster and a reddish-brown color.

13. Manganic Acid.—Manganic acid, H_2MnO_4, has not been obtained, but salts of the acid, called manganates, are known. The manganates are green in color and their solutions are unstable except in the presence of considerable free alkali. Treated with carbon dioxide or made slightly acid, they are converted into the corresponding permanganate. In an alkaline solution the manganates are powerful oxidizing agents.

14. Potassium Manganate.—Potassium manganate, K_2MnO_4, is prepared by fusing a mixture of manganese dioxide and caustic potash, thus:

$$3MnO_2+2KOH=K_2MnO_4+Mn_2O_3+H_2O$$

In the presence of an oxidizing agent the sesquioxide is converted into the manganate.

Potassium manganate is a green-colored mass soluble in water.

15. Sodium Manganate.—Sodium manganate, Na_2MnO_4, is formed in the same manner as the potassium salt, and crystallizes with 10 molecules of water, the formula being $Na_2MnO_4.10H_2O$. This solution is used as a deodorizer and for disinfecting purposes.

16. Permanganic Acid.—Permanganic acid, $HMnO_4$, is prepared by the addition of sulphuric acid to barium permanganate, or by the electrolysis of potassium permanganate. It is a deep-red liquid having a bitter metallic taste and decomposes readily under the action of light or heat.

17. Potassium Permanganate.—Potassium permanganate, $KMnO_4$, is prepared by heating to dull redness a mixture of manganese dioxide, potassium hydroxide, and potassium chlorate. The dark-green mass obtained is leached with boiling water and the solution is filtered and allowed to crystallize. The crystals are dark violet, almost black prisms, with a steel-blue metallic luster, and have a sweet taste with an astringent after taste. They have a specific gravity of 2.7, are soluble in 16 parts of water, forming a deep purple-colored solution, and decompose at 240° C.

Potassium permanganate is a powerful oxidizing agent, its solution being bleached by substances such as ferrous salts, etc., these substances being raised to a higher valence in the process. The action of ferrous sulphate on potassium permanganate breaks the permanganate up into potassium sulphate and manganese sulphate, while the ferrous sulphate is oxidized to ferric sulphate, according to the following equation:

$$2KMnO_4+10FeSO_4+8H_2SO_4=K_2SO_4+2MnSO_4$$
$$+5Fe_2(SO_4)_3+8H_2O$$

Organic substances, especially the offensive emanations from putrescent organic matter, are readily oxidized by potassium permanganate. Like sodium manganate, it is extensively used as a disinfecting agent.

18. Sodium Permanganate.—Sodium permanganate, $NaMnO_4$, is prepared in a manner similar to the potassium salt. It is distinguished from the latter by its being deliquescent. Being cheaper than potassium permanganate, it is frequently used instead of the more expensive salt.

IRON-COBALT-NICKEL GROUP

GENERAL DISCUSSION

19. Iron, cobalt, and nickel are closely related elements. The group as a whole is also related in some respects to the elements chromium and manganese.

20. Iron, like manganese, forms two series of salts: the ferrous salts, in which it appears to be divalent; and the ferric salts, in which it appears to be trivalent. The ferric compounds are the more stable; the ferrous compounds when allowed to stand are usually changed to the ferric condition by the oxidizing action of the air. Iron also resembles chromium and manganese by forming ferric acid, which is analogous in composition to chromic and manganic acids. Cobalt and nickel resemble iron by forming two series of salts corresponding to the two series formed by iron; but their tendency to form salts in which the metals act as bivalent elements is much stronger than is their tendency to form salts in which they appear to be trivalent. The salts of trivalent nickel are very few. There is considerable difference of opinion as to whether the compounds of iron should be written with the single or double formula. That is, for instance, whether ferrous and ferric chlorides should be written $FeCl_2$ and $FeCl_3$ or Fe_2Cl_4 *and* Fe_2Cl_6, respectively. In the case of ferric chloride there seems to be some

evidence in favor of the double molecule, but it is by no means conclusive, and as there is no definite evidence, it is just as well to use the simpler formula, as this is what probably takes part in the reactions at all events. The same applies to cobalt and nickel.

21. Iron, cobalt, and nickel are found closely associated in nature. When pure each metal is nearly white in color. They are very hard and possess high melting points. All of them have pronounced magnetic properties.

IRON

Symbol Fe. Atomic weight 55.84

22. History and Occurrence.—The importance of iron in our industrial and entire economic life is so apparent that only a passing reference to the fact is necessary. It has been of great importance to all civilizations, but it is of relatively greater importance to our own times and development than it has been to any previous period in the world's history. So far as is now known, no metal could be substituted for iron even if it were available in sufficient quantity. The reason is that many of the physical properties of iron and its alloys can be supplied by no other metal or combination of metals.

23. For practical purposes, the perfectly pure material has no value compared with the comparatively impure commercial forms used. This is fortunate because it is both difficult and expensive to obtain the pure metal on a large scale. Furthermore, the presence of certain other elements is required in order to give the combination certain necessary properties that greatly improve it or better adapt it to important uses. The most essential element, as an addition to iron to furnish commercially valuable products, is carbon.

24. Iron is known to have been used in very early times. Although copper and bronze are held by some authorities to have preceded the use of iron, there is abundant evidence of the greater antiquity of iron. It is the belief of some authori-

ties that the use of iron antedated that of copper or bronze, because the process of extracting the former metal was simpler than that involved in extracting and alloying copper and tin.

Iron was undoubtedly first used in Western Asia and adjacent parts of Northern Africa, its history being coexistent with that of the human race and going back beyond the beginnings of authentic history. Accounts of the use and manufacture of iron, doubtless on a small scale, exist in the records of the Egyptians.

It is of interest to note that some of the ancient sources of supply are of considerable importance in modern times. Elba, off the west coast of Italy, furnished ore for the iron industries of Greece and Rome, and in the present generation it has exported ore to European countries and the United States. Algeria is an important source of ore supply for France, and it was also the basis of the iron industry of Carthage in the earliest times.

25. After aluminum, iron is the most abundant metal on or in the earth, and so far as known, the mean composition of the lithosphere, or the crust of the earth, consists by weight of 47.07 per cent. of oxygen, 28.06 per cent. of silicon, 7.90 per cent. of aluminum, and 4.43 per cent. of iron. These four elements constitute seven-eighths of the weight of the earth, iron being the fourth in abundance. Iron is universally distributed both geographically and geologically. However, when iron is compared with aluminum, the somewhat analogous metal in the clay deposits, the concentrations, or workable ore deposits, are relatively limited.

26. Among the more important minerals in which iron is found may be mentioned hematite, Fe_2O_3; magnetite, Fe_3O_4; limonite, or brown hematite, $2Fe_2O_3{\cdot}3H_2O$, or $Fe_4O_3(OH)_6$; siderite, $FeCO_3$; pyrite, FeS_2; and pyrrhotite, Fe_7S_8. It also occurs in many silicates, to which it usually imparts a red color. Of these, hematite, magnetite, limonite, and siderite are used as ores.

These ores are frequently associated with extraneous minerals that injure the quality of the iron. It is worthy of notice

that hardly any of these ores are entirely free from sulphur and phosphorus, substances that not only have a serious effect on the quality of the iron extracted from the ores, but also by their presence in the iron increase the difficulty of obtaining it in a marketable condition.

27. Preparation and Properties.—Pure iron may be prepared by the reduction of iron salts, such as the oxalate, $Fe_2(C_2O_4)_3$, and the chloride, $FeCl_2$, in a stream of hydrogen. It may also be prepared by electrolysis. For pharmaceutical purposes, it is prepared by reducing its oxide by hydrogen at red heat. In this way it is obtained as a black powder, which burns when heated in contact with air.

Pure iron is brilliant silver white in color, softer than wrought iron, capable of receiving a high polish, strongly magnetic, of specific gravity 7.8, and crystallizes in the regular system. In its purest form, iron has a greater tenacity than any other metal, except nickel and cobalt. Its ductility is very great and when heated iron may be rolled into sheets scarcely thicker than paper. At a full red heat iron becomes pasty like wax, and it may then be welded. It melts at a temperature of about 1,530° C.

28. Iron combines directly with the halogens. At ordinary temperatures it combines with the oxygen of the air and exhibits the phenomenon known as the *rusting* of iron. At red heat it combines with carbon and sulphur and decomposes steam.

Iron is acted upon by dilute hydrochloric and sulphuric acids and other dilute acids, hydrogen being evolved and the iron salt of the acid formed. Iron dissolves in hot, moderately dilute nitric acid to form ferric nitrate, $Fe(NO_3)_3$, and nitric oxide:

$$Fe+4HNO_3=Fe(NO_3)_3+NO+2H_2O$$

In cold, dilute nitric acid, ferrous nitrate and ammonium nitrate are formed:

$$4Fe+10HNO_3=4Fe(NO_3)_2+NH_4NO_3+3H_2O$$

Iron, in contact with concentrated nitric acid changes over to the so-called passive state and the acid has no further action

on it. The reason for this behavior is not known, but it has been assumed to be due to the fact that a film of oxide forms on the surface of the iron which protects it from further action.

COMMERCIAL MANUFACTURE OF IRON AND STEEL

29. Blast Furnace.—That variety of commercial iron known as pig iron is manufactured on an enormous scale by the reduction of iron oxide in the blast furnace.

As shown in Fig. 1, this furnace consists of a riveted steel-plate shell *h* lined with firebrick. The shaft is usually divided into four parts, namely, the hearth *a*, which extends to a point just above the level of the tuyères *j* (pronounced *tweers*), through which the air enters; the bosh *b*; the belly *c*, and the stack *d*.

30. The shell and walls above the bosh rest on a mantle *g*, and are supported by cast-iron columns *f*. These columns, of which there are eight, take the weight of the structure off the lower part of the furnace and leave the bosh and base open for examination and convenient working. In the usual construction the bosh walls are made of brick and are from 18 to 20 inches thick. They are supported by steel hoops, and bronze or copper bosh plates *e* are inserted at intervals around the furnace, as shown in Fig. 1. These bosh plates are hollow and water is kept flowing through them. By this means a large amount of heat is carried away from the bosh and the brickwork is preserved. The cooling plates usually start immediately above the tuyères *j*, and are carried up to the mantle *g*, at the top of the columns.

31. Fig. 2 shows a horizontal section of the bosh, through *i*, Fig. 1, that illustrates the position of the tuyères *j*, the columns *f*, and the iron and cinder notches from which the iron and slag are tapped at regular intervals. There are twelve tuyères in this furnace and, in order to prevent them from overheating and burning out, each one is surrounded by a water-jacket at the point where it passes through the furnace wall. The water used is discharged into the troughs *k*, Fig. 1.

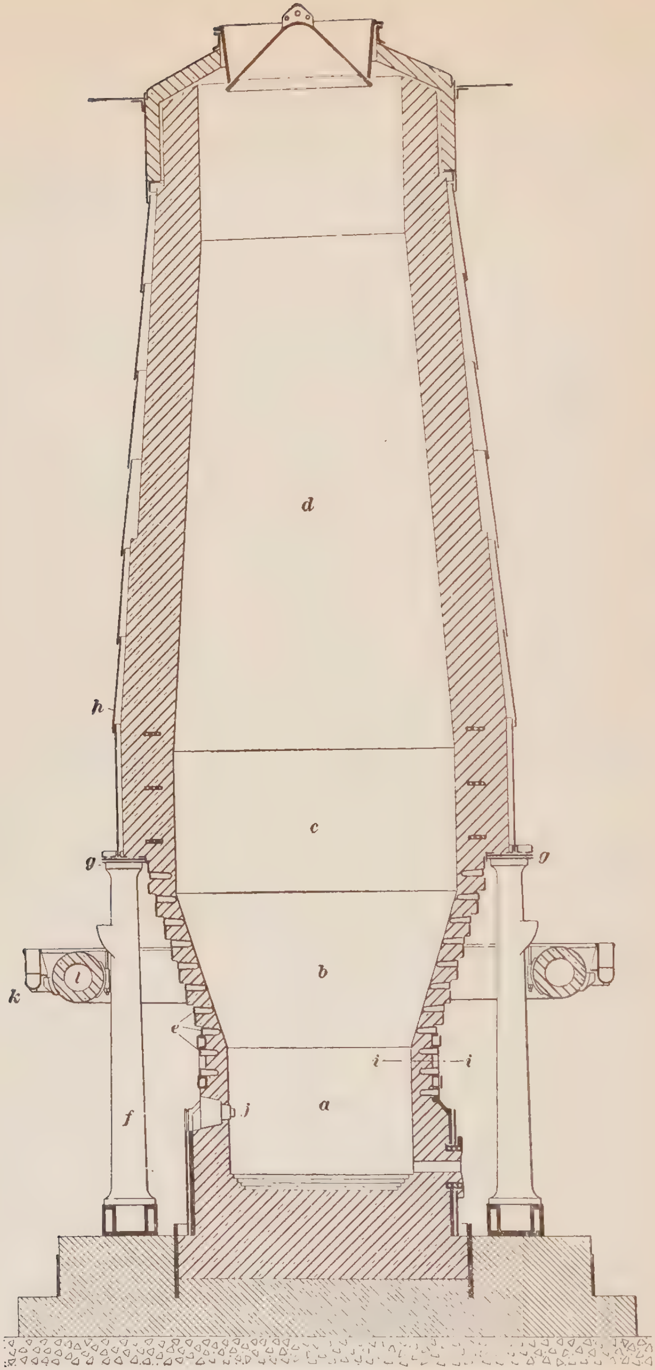


FIG. 1

32. The air blast necessary for the operation of the furnace is supplied by blowing engines. This air before coming to the furnace passes through hot-blast stoves which are heated by burning gas from the furnace in them; this air is usually heated from 480° to 650° C. It is then distributed to the tuyères by means of the bustle pipe *l*, Fig. 1, which encircles the furnace at a height of from 10 to 15 feet from the floor.

33. Operation of the Furnace.—When a new blast furnace has been thoroughly dried out, it is ready for *blowing*

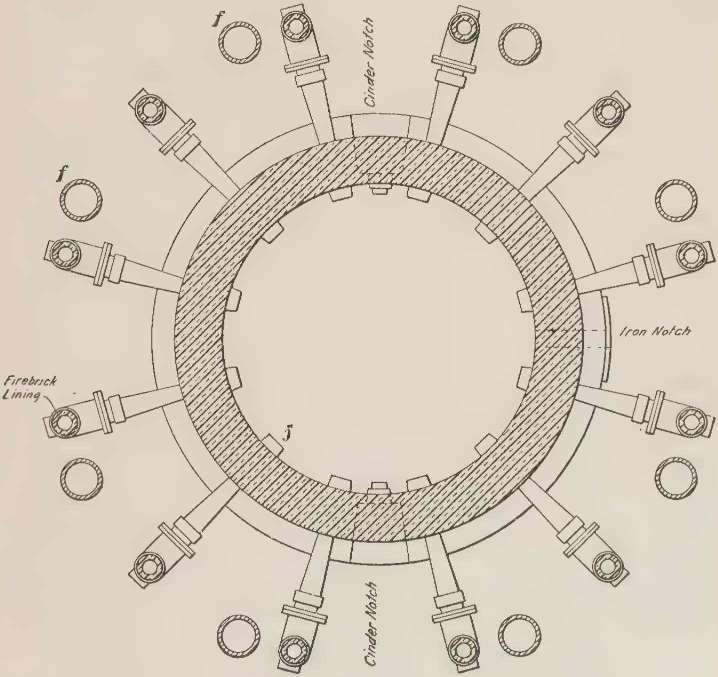


FIG. 2

in, as the process of making it ready for continuous operation is called. A wood fire is first lighted in it and then coke and limestone are introduced before the ore. A gentle blast is then put on and, when the furnace is hot, regular charges of coke, limestone, and ore are introduced at the top. The pressure of the blast is increased and the combustible matter at the high

temperature produced removes the oxygen from the ore, and reduces it to the metallic state. The principal reducing agent is carbon monoxide, in which case the reaction may be written:

$$Fe_2O_3+3CO=2Fe+3CO_2$$

But the reduction is also partially accomplished by means of the carbon of the fuel, in which case the reaction may be represented by the equation:

$$Fe_2O_3+3C=2Fe+3CO$$

34. The limestone unites with the silica and other impurities present in the ore, forming a fusible silicate that collects above the melted iron and is drawn off as cinder or slag. After the iron is reduced to the metallic state it takes up more carbon, becomes fusible, melts, and runs down to the bottom of the furnace, which is called the crucible, or hearth. When enough has collected, it is tapped by drilling through the clay plug that closes the opening. Upon drawing off the molten iron from the furnace or *casting,* as it is called, the iron is allowed to run into molds made in a sand bed and allowed to cool, or the molding is accomplished by means of a casting machine. After this operation, the iron is obtained in pieces about 2.5 feet long and of an irregular thickness of about 5 inches. It is now known as pig iron.

35. The manufacture of iron in the blast furnace is a continuous operation; the materials are constantly added above, and the cinder and melted iron are drawn off from below generally about five times a day, until the furnace needs repairs, or until other reasons put a temporary stop to manufacturing. The frequency with which the iron, as well as the cinder, is drawn off varies in different places and under different conditions; it depends largely on the rapidity with which the iron is being produced.

36. Wrought Iron.—Iron is refined, or converted into wrought iron, by burning out the carbon and silicon, as well as the sulphur and phosphorus; this is effected usually by the process of puddling, or boiling. The pig iron is piled up on the floor of a reverberatory furnace, in contact with some of

the pure ores. On lighting the fire the iron melts and is then continually stirred in order to mix it thoroughly with the oxide. The carbon and silicon are gradually oxidized, the former escaping as gaseous monoxide and the latter being retained as silicate of iron in the slag, until finally the iron becomes pasty and clings together in spongy masses. These are collected into balls, and compacted, first, by working between powerful jaws, called squeezers, and then between rolls, by which the slag is pressed out, and the iron is made into muck bars. The puddled bar is cut into short pieces, made into bundles, heated, and again passed through the rolls; this operation is repeated until the wrought iron is sufficiently pure. By this process the carbon is reduced to one-half of 1 per cent., sometimes to even less, and the other foreign matters to mere traces. If the iron retains phosphorus, it is brittle when cold, and it is called cold-short; if it retains sulphur, it is brittle when hot, or red-short. The iron thus obtained is bluish gray in color, is fibrous in structure, and has a specific gravity of 7.3 to 7.9. Wrought iron is probably the purest form of commercial iron.

37. Manufacture of Steel.—Because of the great variety of steels made today by different processes, it is impossible to give a short definition of the word *steel*. As far as American usage is concerned, however, steel may be in a general way defined as iron that has been treated by one or more of several certain processes. The products included under this name contain from less than .1 to more than 1.5 per cent. of carbon and possess nearly all the chemical and physical properties except those peculiar to cast iron, which belong to the commercial forms of this metal.

38. Several methods may be employed for producing steel. Among these the most important are: (*a*) the cementation process; (*b*) the crucible process; (*c*) the Bessemer process; (*d*) the open-hearth process; and (*e*) the electric-furnace process. Only the four last-mentioned processes are of commercial importance in this country today, the cementation process having been entirely superseded.

39. Cementation Process.—The cementation process consisted in heating wrought-iron bars with charcoal, thus causing them to take up a portion of the carbon. A vertical cross-section of the furnace used is shown in Fig. 3. The iron bars are packed in charcoal, in square, firebrick boxes which are built into the furnace shown in the figure, the whole covered with sand to exclude the air, and heated to redness for from 7 to 10 days, after which it is allowed to cool down slowly. The bars are now brittle, covered with blisters, and easily fusible. They may be at once piled together, heated, and rolled into bars of shear steel, or they may be broken into small pieces, melted in crucibles of fireclay, with the addition of a little manganese dioxide, and cast into ingots; these ingots

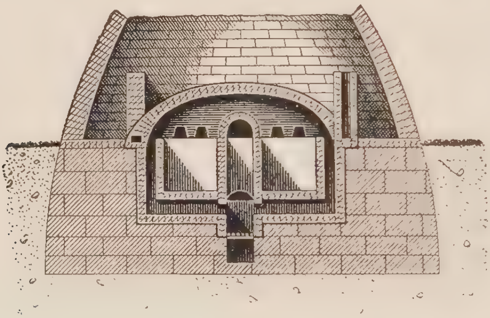


Fig. 3

are afterwards drawn out under the hammer into bars. In this form it is known as cast steel.

40. Crucible Process.—The crucible process is the oldest and simplest of the four principal methods of steel making. It consists essentially of melting scrap iron and steel with the addition of other materials in a crucible constructed from suitable materials.

In the early history of the process, the crucibles were placed on a bed of coke or anthracite coal laid on the bottom of a vertical furnace. At the present time, probably all crucible-steel melting furnaces are of the Siemens regenerative gas type.

41. By the term *regeneration,* as applied to gas furnaces, is meant the storing up of the heat of the waste gases in such

a manner that the air used for combustion is always preheated. By this means a very much higher temperature is obtained than is otherwise possible and a greater economy of fuel is likewise effected. Thus, in this type of furnace the products of combustion escape through a network of firebrick so arranged as to offer the greatest possible contact surface. This part of the furnace is called the *checker-work* because of its design and when the checker-work becomes highly heated by reason of the waste products escaping through it, these products are passed through another chamber containing checker-work through which the air blast has been passing, and the air blast is switched to the hot checker-work. A crucible furnace may contain from two to twenty holes, taking four or six crucibles each. Each hole has its own gas and air regenerators, so that it is practically a separate furnace, but all the holes of a furnace have a common stack and main flues. It is common practice to build four chambers, two at each end, one for gas and the other for air, in each furnace. Each chamber is connected at the bottom with suitable flues, which have valves controlling the gas and air supply, so arranged that the currents of gas and air can be reversed at regular intervals, usually of 15 minutes; the incoming supply travels through the regenerators through which the waste gases escaped during the previous interval. This constant reversal of the direction of gas and air, and of the ends at which they are introduced into the furnace, is kept up during the melting.

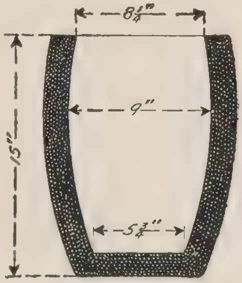


FIG. 4

The crucibles used in this process are made from clay or graphite; the latter kind are almost exclusively used in the United States. Crucibles ordinarily hold from 80 to 125 pounds; the walls are from 1 to 1½ inches thick. The dimensions of a 100-pound crucible are shown in Fig. 4.

42. Crucible Charge.—The materials for making crucible steel are chiefly puddled iron and wrought iron and

steel scrap, together with the necessary amount of carbon, usually charcoal; manganese, as ferromanganese or oxide of manganese, or other additions. Blister steel, made by the cementation process of soaking iron bars with carbon in a converting furnace at a red heat, was originally used, and is even yet to a small extent in America, and quite largely in the original home of crucible-steel making, Sheffield, England. After the crucible has been packed or charged, it is placed in the melting hole by means of tongs.

43. Melting.—With the crucible in the melting hole, a cover is put on it to keep out the gases. The temperature of the furnace is gradually brought up, if a gas furnace, by adjusting the gas and air supply, and draft, if necessary, to give the proper melting conditions. The melting time is generally between 3 and 4 hours, depending on conditions. When the melter judges the charge to be melted, the crucible covers are removed and the contents poured into ingot molds.

44. Superiority of Crucible Steel.—While no fully satisfactory reason has been given for the superiority of crucible over other grades of steel of like composition the causes generally given are: (1) The purer stock melted; (2) as the crucible is covered during the melting, the gases from the fire have very little chance to be absorbed by the metal.

It seems safe to say that to the conditions of melting are principally due the finer quality of crucible steel. In regard to the purer stock, there can be no direct comparison with Bessemer or open-hearth steel, as it is impossible to make either from the usual crucible stock without the use of other materials. But in the crucible process the melting receptacle is closed and all gases are largely kept from the steel, whereas in the Bessemer process the air is blown through the molten metal exposing it to the oxygen and nitrogen of the blast, the solid and gaseous products of combustion, some of which are undoubtedly absorbed, affecting the properties of the steel. In the open-hearth process practically the same conditions may be found, except that the gas for oxidation plays over the surface of the bath.

45. Bessemer Process.—The Bessemer process for the manufacture of steel was invented by Henry Bessemer and patented in England in 1855. The first plant built on a commercial scale was at Sheffield, England, the home of the crucible-steel industry. The first use of Bessemer steel was in certain tools, machine parts, etc., and later in ship building, railroad construction, and the varied kinds of merchant-steel shapes, bars, etc. The great consumption of Bessemer product has been and still is for steel rails. As the process grew in England, it extended to the continent and the United States.

In the Bessemer process, molten pig iron is run into a vessel called a *converter,* which is shown in section in Fig. 5. The converter is made of heavy riveted plate steel and is lined with a refractory material, such as ganister, a high silica rock for the acid process, and dolomite, or magnesite, for the basic process.

46. As shown in Fig. 5, the vessel consists of three principal sections keyed together to form the complete converter which is suspended on trunnions at *d*. The middle, or main, section *b*, around which the trunnion ring *a* extends, holds the body of metal while it is being blown. The bottom *m* is detachable and is held to the body of the vessel by keys and links *l*.

47. Beneath the bottom proper is the tuyère box *f*; its cover *g* is keyed on and is air-tight. The tuyères *j* are spaced over the bottom and supported from below by the tuyère plate *h*; they are placed in position before the bottom is built up, and ganister or dolomite is placed around them. The nose of the converter *c* is also keyed onto the main part, thus permiting its removal for repairs. Converters are made in sizes of from 1 to 20 tons capacity, but blow about 5 tons in small plants and from 10 to 20 tons in the large plants; less than 5 tons is usually for steel-casting plants where the output is limited.

48. Fig. 5 shows the converter in the blowing position. In order to receive the charge of molten pig iron, it is turned in a horizontal position and, while being returned to the vertical, a moderate blast of air is sent through the tuyères. This blast is merely to prevent the molten iron from run-

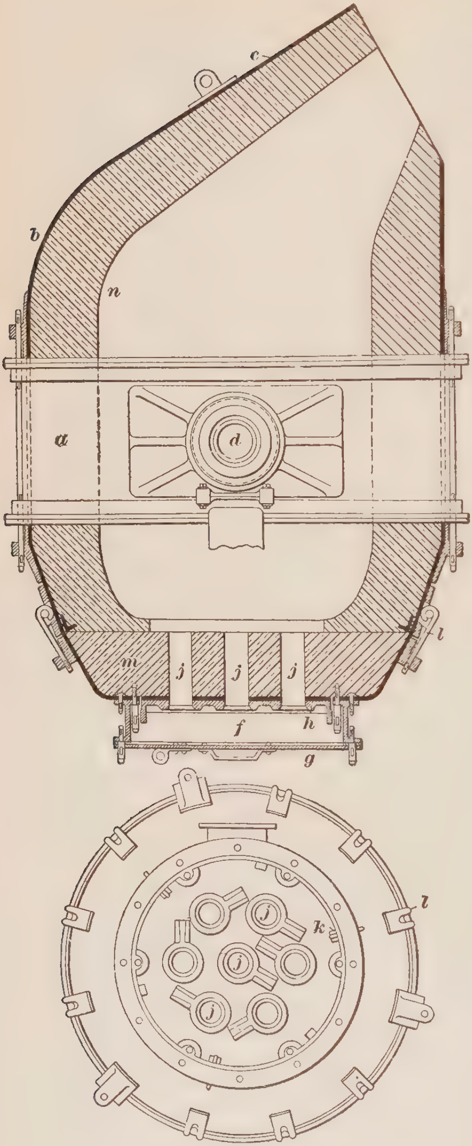


FIG. 5

ning into the tuyères while the converter is being turned to a vertical position. When this position has been reached, the blast is gradually increased to 20 or 30 pounds per square inch. The silicon, manganese, carbon, and a portion of the iron burns in the stream of air, producing a very high temperature which serves to keep the iron in a molten condition. The carbon is converted into carbon monoxide which burns with a long flame at the mouth of the converter and is usually accompanied by a stream of sparks from the combustion of the iron. The blow is continued until the flame of carbon monoxide disappears. If continued longer the combustion proceeds at the expense of the iron. The blast is then lowered in pressure and the necessary amount of spiegeleisen or

ferromanganese added and the blast turned on again for a few minutes, after which the molten steel is run into ingot molds by tilting the converter. This process, as described, requires an iron free from sulphur and phosphorus. If, however, the converter is lined with a basic material, as done by Gilchrist and Thomas, using a calcined dolomite, pig iron containing varying amounts of phosphorus can be used.

49. The Open-Hearth Process.—Steel was first made by the open-hearth process in England in 1862 in the regenerative furnace of the Siemens brothers, which was patented in 1861. This was not the first attempt to make steel on an open hearth, however, many previous experiments having been made, but it was only with the Siemens apparatus, which gives the high temperature necessary, together with an almost perfect control of heat conditions, that success was finally attained.

50. In the open-hearth process a reverberatory furnace built over regenerating flues is used. These flues are heated by the waste gases from the furnace and in turn heat the gas and air passing to the hearth of the furnace. Two forms of this process are in use, namely, the acid, requiring a hearth made of infusible silicious material, and the basic, using a hearth made of dolomite. The latter process is the one most generally used, as pig iron can be converted directly with this modification.

The charge of pig iron, scrap iron, steel, and limestone is melted on the hearth of the furnace by a flame of carbon monoxide raised to a high temperature by the regenerators. When the charge has melted, iron ore, generally hematite, and some limestone are added. A violent boiling now ensues and slag is formed by the silica obtained by the oxidation of the silicon present combining with the ferrous oxide of the ore. The carbon is next removed by oxidizing it to carbon monoxide, and the phosphorus goes into the slag. A test piece of steel is withdrawn and the end of the process determined by the fracture and analysis of this test. When the process is complete the steel is run into a ladle when ferromanganese is added if required to deoxidize and recarbonize, and then the steel is

run into ingots. In modern practice, liquid metal direct from the blast furnaces is used in the place of pig iron.

51. Electric-Furnace Process.—In the electric-furnace process, which is the newest process for the making of steel, numerous types of electric furnaces are used and a great variety of steels are produced.

The Heroult furnace, which was among the first to be developed to the point where its operation was a commercial suc-

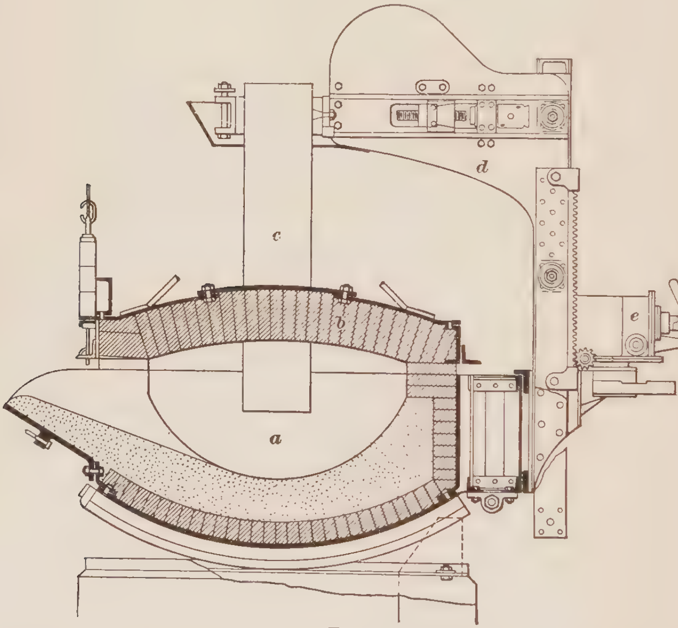


Fig. 6

cess, is probably used to a greater extent today than any other and will therefore be described.

52. A 2.5-ton furnace is illustrated in Fig. 6. It consists of a shallow hearth *a* of dolomite, which is incased in a steel shell and covered with a roof *b*, made of silica brick. There are two 14-inch carbon electrodes *c* projecting into the furnace through the roof. These electrodes are threaded for continuous feeding and are used in either 4- or 6-foot sections. They

are held in place by a steel framework *d*, extending from the rear of the furnace and over its roof. The electrodes may also be raised or lowered by means of the hand wheel shown at *e*.

53. Depending upon the quality of the steel to be produced, the electric furnace is charged with straight carbon or alloy steel scrap, Bessemer steel, wrought iron, or even pig iron. An oxidizing flux of lime and iron ore is then added and the current turned on. Oxidation of the impurities in the metal begins as soon as the scrap becomes pasty, so that by the time the charge is completely melted, the carbon, silicon, phosphorus, and manganese originally contained in the metal is reduced to less than .1 per cent. of each. The slag formed by this operation is removed and deoxidation of the metal is accomplished by adding reducing agents such as ferrosilicon or ferromanganese. The metal is now ready for carburization and the addition of other materials, depending upon the kind of steel to be made, to bring it to the desired composition.

54. For many years, all high-grade steels were manufactured by the crucible process, but since the development of the electric furnace to its present state of efficiency, it has been gradually adopted for steel-refining purposes. It is also stated that any product that can be made by the crucible process can also be made by the electric furnace at less cost. The electric furnace gives a product of low or high carbon content, and alloy steels of exact composition are easily produced. By its use large castings can be made from one furnace, while with the crucible process the contents of a large number of crucibles must be used.

55. Properties of Steel.—As steel is a term applied to a variety of material produced by various processes and differing in chemical composition, its properties cannot be definitely stated, but differ with the different varieties. The so-called mild steel, which contains a low percentage of carbon, is relatively soft and malleable and probably cannot be hardened by any physical treatment. On the other hand, steel that contains more carbon, if heated to a rather high tempera-

ture and suddenly cooled, or quenched, by dipping it in cold water, becomes very hard. A steel containing a high percentage of carbon becomes much harder when treated in this way than one containing a smaller quantity of this element, and those samples containing but mere traces of carbon, as stated before, cannot be hardened to any considerable extent by this process. It thus appears that the property of hardening when suddenly cooled from a high temperature depends largely, if not entirely, on the carbon content of the steel. Careful study and examination of steel under varying conditions have led to the belief that the phenomena attending the hardening and softening of

TABLE I

TEMPERING OF STEEL

Temperature Degrees C.	Color	Implements Tempered
230	Pale straw yellow	Surgical instruments, razors, metal engraving tools
243	Straw yellow	Knives, hammers, metal shears, steel cold chisels
254	Brown	Hatchets, scissors, rock and hard-coal drills
266	Brown-purple	Axes, planes, picks
277	Purple	Wood-turning tools, soft-coal picks, and drills
288	Bright blue	Springs, augers
293	Full blue	Soft-iron cold chisels
316	Dark blue	Spiral springs, hand and power saws

steel by changes of temperature, are due to the forms assumed by the carbon under varying conditions.

56. Osmond holds that there are two allotropic forms of iron, which he calls α and β iron, and that the changes produced by variations in temperature are due to the conversion from one to the other of these forms. This theory, however, is not required to account for the changes observed and is not generally accepted. If a piece of high-carbon steel is heated to a high temperature and quenched, it becomes exceedingly

hard—too hard, in fact, for ordinary purposes. If this is again heated to the same temperature and cooled slowly, it loses its hardness, and assumes the properties it possessed before heating; but if instead of heating to the high temperature used in hardening, it is heated to a much lower temperature and cooled, suddenly as a rule, though not always, its hardness is modified or tempered, but not destroyed. It should be noted that the word tempering is frequently and not altogether incorrectly applied to any heating and sudden cooling of iron.

When the hardened steel is reheated, a thin film of oxide is formed on its surface imparting different colors to the metal, by which its temperature can be judged with considerable accuracy. In Table I, which is compiled from the most reliable sources, the temperature to which steel is heated in tempering it for various instruments is given, together with the color assumed in each case.

57. Alloy Steels.—Manganese, nickel, vanadium, chromium, tungsten, and molybdenum appear to make steel hard in whatever manner it is cooled. Without being heat treated, however, these alloy steels are only slightly superior to plain carbon steels. Manganese steel is very tough and is used when long-continued wear is essential, in the jaws of crushing machines, elevator buckets, etc. Nickel is added to increase the strength and is used chiefly for armor plate, forgings, and castings. It does not affect the ductility of the steel. Vanadium acts in a similar manner to nickel, but less vanadium is required to obtain the same effect. Chromium is used to increase the hardness of surfaces and to resist severe shocks. Tungsten tends to harden the steel and to prevent softening due to increase of temperature. Steels containing tungsten are frequently known as self-hardening steels and are used for high-speed lathe, planing, and boring-mill tools. Molybdenum steels possess properties similar to those of tungsten steels, but they are tougher than the latter. Molybdenum steels are used for some high-grade saws. There are also many alloy steels which contain more than one of these elements.

OXIDES OF IRON

58. Three oxides of iron are known, namely: ferrous oxide, FeO; ferric oxide, Fe_2O_3; ferrous-ferric oxide, Fe_3O_4.

59. Ferrous Oxide and Ferrous Hydroxide.—Ferrous oxide, FeO, may be obtained as a black powder by igniting ferrous oxalate in a closed vessel. Ferrous hydroxide, $Fe(OH)_2$, is formed as a white precipitate when an alkaline hydroxide is added to the solution of a ferrous salt. A white flocculent precipitate is thus produced which, dried away from the air, has a slightly greenish tint, but which on exposure takes fire and burns to ferric oxide. Ferrous oxide has a strong reducing action.

60. Ferric Oxide.—Ferric oxide, Fe_2O_3, which occurs abundantly in nature, is called hematite, and is one of the most important of the iron ores. Artificially it may be prepared by igniting the hydroxide or by calcining ferrous sulphate. This salt first loses its water, and then at red heat decomposes into sulphur trioxide, sulphur dioxide, and ferric oxide:

$$2FeSO_4 = SO_3 + SO_2 + Fe_2O_3$$

A red powder is thus obtained, which is known in commerce under the name of colcothar, rouge, and Venetian red, and is used for polishing metals, glass, etc. Its specific gravity is 5.2. It is reduced to the metallic state when heated in hydrogen.

61. Ferric Hydroxide.—Ferric hydroxide, $Fe(OH)_3$, is prepared by adding ammonium hydroxide to the solution of a ferric salt, when it separates as a brownish-red precipitate, which may be washed and dried at a moderate temperature without decomposing. If, however, it is heated to 100° C., or if the solution containing it is boiled for some time, it gradually loses water, forming the hydroxides $FeOOH$, $Fe_2O(OH)_4$, etc. When strongly ignited, these give up more water and are converted into ferric oxide. The hydroxide $FeOOH$ corresponds to the compounds $AlOOH$ and $CrOOH$, and is believed to form some salts.

62. Ferrous-Ferric Oxide.—Ferrous-ferric oxide, Fe_3O_4, is found in nature as the mineral magnetite, and is believed to be a combination of the oxides of iron, FeO and Fe_2O_3. Ferrous-ferric oxide is formed when iron is burned in oxygen, or when steam is passed over red-hot iron.

The very stable character of Fe_3O_4 has permitted its application for protecting iron from rust. When superheated steam is passed over the red-hot metal, a very dense, strongly adhering film of Fe_3O_4 is produced, which effectually protects the metal. A similar coating is produced by the action of a mixture of air and carbon dioxide.

63. Ferric Acid.—Ferric acid, H_2FeO_4, while not known in the free state, forms ferrates, some of which are fairly well known. A solution of the potassium salt is formed when iron filings and potassium nitrate are strongly ignited, and the fused mass is extracted with water. The solution has a fine purple color. It can be prepared also by passing chlorine through a strong solution of caustic potash containing freshly precipitated ferric hydroxide in suspension. Potassium ferrate forms a black precipitate insoluble in alkaline solutions but soluble in water. It is very unstable. The solution decomposes on boiling with an evolution of oxygen, and precipitation of ferric hydroxide.

The ferrate of barium is prepared by adding barium chloride to a solution of either potassium or sodium ferrate. It is a dark-red powder, soluble in acetic acid, and fairly stable.

64. Ferrous Carbonate.—Ferrous carbonate, $FeCO_3$, occurs in nature as siderite, or spathic iron ore, in obtuse rhombohedrons, light grayish or yellowish in color, and of specific gravity 3.8. It is thrown down on the addition of a soluble carbonate to a solution of a ferrous salt, as a white precipitate, rapidly passing into brown ferric hydroxide. It is soluble in water containing carbonic acid and is found in this state in nature in the waters of chalybeate springs.

SULPHIDES OF IRON

65. Iron Disulphide.—Iron disulphide, FeS_2, being widely diffused, as iron pyrites, is the most important of the sulphides of iron. It occurs in nature in two distinct forms: one, brass-yellow and isometric, is known as pyrite; and the other, white or dull greenish-yellow and orthorhombic, is called marcasite. This latter variety can be altered much more readily than the other and possesses a great tendency to attract oxygen from the air and become converted into sulphate. When heated in closed vessels, pyrite loses a part of its sulphur. Iron disulphide may be obtained artificially by heating iron with excess of sulphur to a temperature below redness, or by heating ferric oxide or hydroxide moderately in a stream of H_2S as long as it increases in weight.

66. Ferrous Sulphide.—Ferrous sulphide, FeS, is found in small quantities in many meteorites. It may be produced by the direct union of iron and sulphur, as when iron wire burns in sulphur vapor, or when the two substances are melted together in suitable proportions. It is a grayish-yellow solid with a metallic luster and crystalline structure, and is easily fusible. When finely divided, it is oxidized to ferrous sulphate on exposure to the air. With acids it evolves hydrogen-sulphide gas. It is precipitated from ferrous solutions by alkaline sulphides.

67. Ferric Sulphide.—Ferric sulphide, Fe_2S_3, may be prepared by heating iron and sulphur mixed in the proper proportions. It is not commercially important, and is interesting, theoretically, principally because it is analogous to Fe_2O_3.

CHLORIDES OF IRON

68. Ferrous Chloride.—When hydrochloric-acid gas is passed over iron filings heated to redness, ferrous chloride, $FeCl_2$, is obtained in white, shining, hexagonal scales that have a specific gravity of 2.5 and are deliquescent in moist air. It is soluble in 2 parts of water, and the solution evaporated and

cooled away from the air, deposits crystals having the composition $FeCl_2 \cdot 4H_2O$. When heated in the air to drive off the water, these crystals decompose. Ferrous chloride may be prepared in solution by dissolving iron in hydrochloric acid away from air. If the solution containing hydrochloric acid is exposed to air, the chloride will be oxidized to ferric chloride; but if the solution does not contain hydrochloric acid, it breaks up into ferric chloride, which remains in solution, and a basic chloride, which separates as a precipitate. Ferrous chloride unites with the chlorides of the alkalies, forming double chlorides of the composition K_2FeCl_4, Na_2FeCl_4, etc.

69. Ferric Chloride.—Ferric chloride, $FeCl_3$, is most readily prepared in solution by dissolving iron in hydrochloric acid, and saturating the solution with chlorine. This solution, especially if dilute, is decomposed into hydrochloric acid and an insoluble oxychloride when strongly heated. By treating the solution carefully, yellow crystals of $FeCl_3 \cdot 6H_2O$ may be obtained. These are decomposed into ferric oxide and hydrochloric acid if heated to drive off the water. The anhydrous chloride is obtained by heating iron in an atmosphere of chlorine.

SULPHATES OF IRON

70. Ferrous Sulphate.—Ferrous sulphate, $FeSO_4$, long known under the names of copperas and green vitriol, is prepared by dissolving iron in dilute sulphuric acid. It is obtained as a by-product in the manufacture of copper sulphate. Ferrous sulphate crystallizes in fine, green, monoclinic crystals, having the composition $FeSO_4 \cdot 7H_2O$ and a specific gravity of 1.9.

Ferrous sulphate dissolves readily in water and forms a pale-green solution. If this solution is heated, or upon long standing, it decomposes, forming a muddy solution, due to the oxidation of the sulphate and the formation of a basic sulphate. Ferrous sulphate readily absorbs oxygen and, hence, is frequently used as a reducing agent. In this capacity it is frequently used to precipitate gold in the metallic state from its

solutions. Its principal use, however, is for the preparation of iron mordants for the dyeing industries, inks, Prussian blue, tanning, etc.

71. Ferric Sulphate.—Ferric sulphate, $Fe_2(SO_4)_3$, is obtained by treating a solution of ferrous sulphate containing sulphuric acid with an oxidizing agent, or by dissolving ferric hydroxide in sulphuric acid and evaporating the solution. It is a slightly yellowish mass that dissolves completely though rather slowly in water. The solution is yellow-brown and has an acid reaction. When concentrated by evaporation, it deposits a deliquescent, yellowish, crystalline mass of hydrated ferric sulphate.

Ferric sulphate unites with sulphates of the alkalies, forming double sulphates that are analogous to alum, and are known as *iron alums*. The potassium salt has the composition $Fe_2(SO_4)_3K_2SO_4{\cdot}24H_2O$.

72. Iron Phosphates.—Ferrous phosphate, $Fe_3(PO_4)_2$, occurs in nature with 8 molecules of water of crystallization, as the mineral vivianite. It may be precipitated from a ferrous solution by adding sodium phosphate.

Ferric phosphate, $FePO_4$, separates as a precipitate when sodium phosphate is added to a ferric solution.

COBALT

Symbol Co. Atomic weight 58.97

73. History and Occurrence.—The property which certain cobalt compounds possess of coloring glass blue was known to the ancients. The ores were long known to the German miners under the name of cobalt, a name derived from *kobold,* meaning a roguish spirit who, as they supposed, offered them an ore rich in appearance but otherwise worthless. Brandt in 1735 prepared the metal and his observations on its properties were confirmed by Bergman in 1780.

Cobalt does not occur free in nature except in meteoric iron. It usually occurs as linnæite, $(CoNiFe)_3S_4$; speiss cobalt,

$CoNiFeAs_2$; skutterudite, $CoAs_3$; smaltite, $CoAs_2$; and cobaltite, $CoAs_2.CoS_2$.

74. Preparation and Properties.—Cobalt ores containing sulphur and arsenic are roasted and the roasted ores fused with lime or sand. The iron in the ore enters the slag, and the cobalt, in the form of speiss, that is, combined with arsenic, sinks. The speiss is dissolved in hydrochloric acid, when any arsenate of iron is precipitated by means of bleaching powder and calcium hydroxide. The clear supernatant liquid is drawn off and the heavy metals, copper, bismuth, etc., precipitated with hydrogen sulphide. Bleaching powder is added to the clear liquid remaining and the cobalt is precipitated as an oxide.

Metallic cobalt is prepared by igniting the oxide or the chloride in a current of hydrogen; by the electrolysis of the chloride; or by ignition of the chloride with sodium or potassium. It can be prepared also by heating the oxalate under powdered glass.

Cobalt is a silver-white metal, slightly tinged with red. It is harder than either iron or nickel, malleable, very ductile and magnetic. It melts at 1,478° C., has a granular fracture and a specific gravity of 8.7. The compact metal does not change at the ordinary temperature, but the powder oxidizes very readily in the air. It is only slowly soluble in sulphuric and hydrochloric acids, evolving hydrogen, but is readily soluble in nitric acid.

COMPOUNDS OF COBALT

75. Cobalt forms three oxides: cobaltous oxide, CoO; cobaltic oxide, Co_2O_3; and cobaltous-cobaltic oxide, Co_3O_4.

76. Cobaltous Oxide.—Cobaltous oxide, CoO, is obtained when one of the higher oxides is heated in a current of hydrogen or of carbon dioxide. It is prepared also by heating cobaltous hydroxide in the absence of air. It is a decidedly basic oxide, is a light-brown powder unaffected by the air at ordinary temperatures, and dissolves in acids, forming cobaltous salts. Heated in the air, it forms cobaltous-cobaltic oxide.

77. Cobaltic Oxide.—Cobaltic oxide, Co_2O_3, is obtained as a black powder when the nitrate is gently heated. It acts as a feeble base and is soluble in acids, when it forms the cobaltic salts, which are unstable. When heated it yields the cobaltous-cobaltic oxide.

78. Cobaltous-Cobaltic Oxide. — Cobaltous-cobaltic oxide, Co_3O_4, is formed when any of the oxides or the nitrate is ignited in the air. It is a black powder, is used for the preparation of cobalt products and for painting on porcelain. Boiled with hydrochloric acid, it forms cobaltous chloride and evolves chlorine. It is analogous to Fe_3O_4 and is believed to be a combination of the oxides CoO and Co_2O_3.

79. Cobaltous Hydroxide.—Cobaltous hydroxide, $Co(OH)_2$, is the precipitate obtained when potassium hydroxide is added in excess to a boiling solution of a cobaltous salt. A blue precipitate of a basic salt is first obtained, and this, on continued boiling, becomes converted into the rose-red hydroxide. This readily absorbs oxygen from the air, changing to the brown cobaltic hydroxide. Cobaltic hydroxide, $Co(OH)_3$, is obtained as a brownish-black precipitate when an alkaline hypochlorite solution is added to a solution of a cobalt salt.

80. Cobaltous Nitrate.—Cobaltous nitrate, $Co(NO_3)_2$, can be prepared by dissolving cobaltous oxide in nitric acid, as

$$CoO+2HNO_3=Co(NO_3)_2+H_2O$$

It forms red, deliquescent crystals having the composition, $Co(NO_3)_2 \cdot 6H_2O$, that are easily soluble in water and melt somewhat under 100° C., changing from red to blue when the water of crystallization has been expelled. On further heating it is converted into cobaltic oxide. It is used largely as a blowpipe reagent.

81. Potassium-Cobaltic Nitrite.—When a solution of cobaltous nitrate is acidified with acetic acid and a solution of potassium nitrite is added, a yellow precipitate of potassium-cobaltic nitrite, or cobalt yellow, $K_6Co_2(NO_2)_{12}$, is obtained. It forms a yellow microcrystalline powder slightly soluble in water.

82. Cobaltous Chloride.—Cobaltous chloride, $CoCl_2$, is prepared by heating the powdered metal in chlorine gas, or by dissolving one of the oxides or the carbonate in hydrochloric acid. It crystallizes in red prisms with 6 molecules of water. Heated to 120° C., these crystals change to the blue color of the anhydrous salt. A solution of cobaltous chloride forms the so-called *sympathetic ink*, for characters written with its pink solution are almost invisible until exposed to heat, when they become blue and on exposure to the air gradually resume their original pink color.

83. Cobaltous Sulphide.—By adding ammonium sulphide to a solution of a cobalt salt, a black precipitate of cobaltous sulphide, CoS, is obtained. It differs from ferrous sulphide in being insoluble in dilute hydrochloric acid.

84. Cobaltous Sulphate.—Cobaltous sulphate, $CoSO_4 \cdot 7H_2O$, occurs native as the mineral bieberite. It is prepared by dissolving the oxides or the carbonate in sulphuric acid. It crystallizes in red prisms isomorphous with ferrous sulphate, is not affected by the air, is soluble in water, has a weak, astringent,. metallic taste, and is insoluble in alcohol. It is used for the manufacture of cobalt salts, and in decorating porcelain. It does not acquire a blue color when dried and can be submitted to a high temperature without undergoing decomposition.

85. Cobaltous Arsenate and Diarsenide.—Cobaltous arsenate, $Co_3(AsO_4)_2$, occurs as cobalt bloom in violet needles containing 8 molecules of water of crystallization. It is soluble in dilute mineral acids. The diarsenide, $CoAs_2$, occurs as smaltite, or speiss cobalt, associated with iron and nickel.

NICKEL

Symbol Ni. Atomic weight 58.68

86. History and Occurrence.—Nickel was discovered by Cronstedt in 1751 in a copper-colored mineral to which, having failed in attempting to extract copper from it, the

miners had applied in derision the name *kupfernickel*, and from which name nickel has been derived. Except in meteoric irons nickel does not occur native, but is a constituent of many minerals. It occurs as niccolite, $NiAs$; nickel glance, $NiAsS$; ullmannite, $Ni_2S_2(AsSb)_2$; annabergite, $Ni_3(AsO_4)_2{\cdot}8H_2O$; and garnierite, $2(NiMg)_5Si_4O_{13}{\cdot}3H_2O$.

87. Preparation.—The sulphide ores containing nickel are first roasted to remove the excess of sulphur and to oxidize the iron, after which the ore is smelted in a blast furnace. This produces a matte containing from 35 to 40 per cent. of nickel and copper. This matte is then concentrated to a matte containing 70 to 80 per cent. of nickel and copper, either in a blast furnace or by means of a converter. The nickel is separated from the copper and the small amount of iron still remaining in the matte by fusion with sodium sulphate and coke in a magnesia-lined, open-hearth reverberatory furnace. While in a molten condition in this furnace the charge is poled frequently for about 5 hours. Sodium sulphide is formed and this dissolves the copper and iron sulphides, and the nickel sulphide is tapped into molds. The nickel sulphide is roasted with sodium nitrate, the oxide obtained is washed, dried, and pressed into cubes with powdered charcoal and strongly ignited in clay crucibles on the hearth of a reverberatory furnace. A furnace in which this reduction can be carried on continuously has been devised and is replacing the reverberatory furnace. This furnace has vertical tubes of fireclay passing through it. The tubes are charged at the top with the nickel oxide and charcoal and the metal is drawn off at the bottom.

Another method, known as the gas method, consists of exposing the roasted matte to the action of water gas or producer gas at a temperature of about 400° C. The reduced metal is then exposed to a current of carbon monoxide and forms nickel carbonyl, $Ni(CO)_4$. This is then passed through chambers heated to 180° C., in which the nickel is deposited.

88. Properties.—Pure nickel is a pure silver-white metal having a specific gravity of 8.9. It is capable of taking a high polish and is malleable and ductile. It does not oxidize

in dry or moist air at ordinary temperatures, melts at 1,452° C., and distils in the electric furnace. It is magnetic but loses its magnetism when heated.

Nickel is used for various industrial purposes. The steel and plating industries consume the most of the nickel produced. Small quantities are used in the manufacture of laboratory and cooking utensils. Alloys of nickel are used in coinage, jewelry, boiler and condenser tubes, and for scientific apparatus.

89. Alloys of Nickel.—Nickel with a great many metals forms some very important and useful alloys. Among the most important are:

Aluminum nickel is composed of 28 to 30 per cent. of aluminum and from 40 to 72 per cent. of nickel. It is used for cheap jewelry. Nickel slightly hardens and toughens aluminum.

Chrome nickel is used for making high-speed tool steel. It contains 73 per cent. of chromium, 23 per cent. of nickel, 2.5 per cent. of iron, 1 per cent. of carbon, and .5 per cent. of silicon.

Molybdenum nickel is also used to alloy with steel and usually contains 40 to 75 per cent. of molybdenum, 20 to 50 per cent. of nickel, 2 to 2.5 per cent. of iron, 1 to 1.5 per cent. of carbon, and from .25 to .5 per cent. of sulphur.

Invar is an alloy of iron and nickel containing 36 per cent. of nickel and 64 per cent. of iron. It is used for the manufacture of measuring instruments. The valuable property of this alloy lies in the fact that it has no expansion when heated.

Above 36 per cent. of nickel, the nickel iron alloys are influenced by temperature, the coefficient of expansion increasing with the proportion of nickel.

Platinite, which is an iron-nickel alloy containing 42 per cent. of nickel, has the same coefficient of expansion as glass and is used for making armored glass.

Ferro-nickel, which is an iron compound containing from 25 to 75 per cent. of nickel, is used to increase the elasticity and tenacity of steel. It is used in the manufacture of steel for armor plates, guns, etc.

Constantan is the trade name for an alloy used largely for the manufacture of resistance devices for electrical work. It contains 40 per cent. of nickel and 60 per cent. of copper.

German silver, which consists of 50 to 60 per cent. of copper, 20 to 30 per cent. of nickel, and from 20 to 30 per cent. of zinc, is a silvery-white compound used in the manufacture of jewelry, scientific instruments, resistance wires, etc.

Monel metal, which is an alloy of 3 parts of nickel to 1 part of copper, is obtained from the copper-nickel deposits of the Sudbury, Canada, district. It has a silver-white color and takes a high polish; it has a high melting point, great tensile strength, and resists corrosion, particularly by the strong acids.

Alloys of copper with nickel and zinc, or with nickel alone, are used in the United States, Germany, Belgium, and Switzerland for the manufacture of small coins. The advantages of nickel coins are: (1) nickel being of greater value than copper, the coins can be made smaller for the same value, and consequently they are more convenient to handle; (2) the alloy is hard and therefore wears well; and (3) its manufacture not only requires skilled workmen, but also powerful machines, which facts offer a certain safeguard against counterfeiting.

COMPOUNDS OF NICKEL

90. Nickelous and Nickelic Oxides.—Nickelous oxide, NiO, and nickelic oxide, Ni_2O_3, are known. Nickelous oxide is an ash-gray powder that is obtained by strongly igniting the nitrate or carbonate of nickel. On adding potassium hydroxide to a solution of a nickel salt, an apple-green precipitate of nickelous hydroxide, $Ni(OH)_2$, is formed. When heated, this is converted into nickelous oxide.

Nickelic oxide, Ni_2O_3, is a black powder prepared by the careful ignition at a low temperature of the nitrate or carbonate. Nickelic hydroxide, $Ni(OH)_3$, is precipitated as a black powder when the solution of a nickel salt is treated with sodium hypochlorite.

$$4NiSO_4+8NaOCl+6H_2O=4Ni(OH)_3+4Na_2SO_4+4Cl_2+O_2$$

As nickelic oxide and hydroxide are the only compounds in which nickel acts as a trivalent element, the endings *ous* and *ic* are seldom used in speaking of the other compounds of nickel.

91. Nickel Chloride.—Nickel chloride, $NiCl_2$, may be obtained anhydrous by the action of chlorine on nickel filings; it is volatile at a dull-red heat and sublimes in golden-yellow scales. It may be obtained in solution by the action of boiling water on the anhydrous salt, or by the action of hydrochloric acid on either oxide or carbonate of nickel. Its solution is green and after proper concentration deposits beautiful green crystals having the composition $NiCl_2{\cdot}6H_2O$.

92. Nickel Sulphate.—Nickel sulphate, $NiSO_4$, is deposited in fine emerald-green prisms having 7 molecules of water isomorphous with magnesium sulphate, when its solution is allowed to evaporate spontaneously below 15° C. There is another sulphate containing 6 molecules of water that is dimorphous. When deposited between 20° and 30° C. it crystallizes in octahedrons, but when its solution is made to crystallize between 60° and 70° C., monoclinic crystals are obtained isomorphous with the corresponding sulphates of zinc and cobalt. Nickel sulphate dissolves in three times its weight of water at 10° C.

93. Nickel Ammonium Sulphate.—Nickel ammonium sulphate, $(NH_4)_2SO_4{\cdot}NiSO_4{\cdot}6H_2O$, used in nickel-plating, is prepared by dissolving pure nickel in dilute sulphuric acid and adding ammonium sulphate to the solution. The crystalline paste formed is purified by recrystallization. It forms green, monoclinic prisms somewhat soluble in water.

94. Nickel Sulphide.—Nickel sulphide, NiS, is obtained as a black precipitate by the action of an alkaline sulphide on a salt of nickel; it is insoluble in HCl, but ammonium disulphide dissolves it to a dark-brown liquid.

95. Nickel Carbonyl.—Nickel carbonyl, $Ni(CO)_4$, is obtained when carbon monoxide is passed over metallic nickel at a temperature of about 100° C. It is a colorless liquid boiling at 43° C.; it solidifies at −25° C. and forms needle-

shaped crystals. It is soluble in alcohol, benzine, and chloroform, but is insoluble in dilute acids or alkalies. Its vapor decomposes at 150° to 180° C. into nickel and carbon monoxide. Chlorine decomposes it according to the equation:

$$Ni(CO)_4+Cl_2=NiCl_2+4CO$$

96. Nickel Carbonate.—Nickel carbonate, $NiCO_3$, is obtained as pale-green rhombohedra when a solution of nickel chloride is heated with calcium carbonate. When a solution of an alkaline carbonate is added to a solution of a nickel salt a pale-green precipitate of a basic nickel carbonate of varying composition is thrown down.

PLATINUM METALS

97. Introductory.—The platinum group consists of six metals which in turn, on the basis of their chemical and physical properties, may be arranged in two sub-groups, one of which contains the metals ruthenium, rhodium, and palladium, and the other, osmium, iridium, and platinum. All of these metals are found in the metallic state. The principal deposits are in the Ural and Caucasus regions of Russia, while smaller deposits are found in California, Brazil, and Australia. The metals all have a silvery luster and are not acted upon by the air at ordinary temperatures. The metals as a class are very resistant to the action of concentrated acids. Thus, while palladium is dissolved by hot concentrated nitric acid, the others are scarcely attacked.

RUTHENIUM

Symbol Ru. Atomic weight 101.7

98. Ruthenium was discovered by Osann in 1828 in the platinum ores from the Ural. Very little was known regarding it until 1846 when Claus investigated the metal. He retained the name ruthenium which had been given to this metal by Osann. It occurs in platinum ores and as the sulphides of ruthenium and osmium in the mineral laurite. Ruthenium is

prepared by igniting the residues left, after extracting the platinum from its ores, in a stream of chlorine in the presence of sodium chloride. The fused mass is dissolved in water, potassium nitrite is added, the solution neutralized with sodium carbonate, and evaporated to dryness. The double nitrites of ruthenium and potassium are extracted with absolute alcohol, leaving any rhodium present in the residue. After adding water to the solution and distilling off the alcohol, the solution is made acid with hydrochloric acid, when a red solution of the double chlorides is obtained. This is treated with sal ammoniac, forming ammonium-ruthenium chloride, after which the ruthenium is precipitated by mercuric chloride, crystallized and ignited when pure ruthenium is obtained.

99. Ruthenium is a hard, heavy, white, brittle metal with a specific gravity of 12.26. With the exception of osmium and iridium, it is the most difficult of the platinum metals to fuse. It can be melted in the electric arc at a temperature above 2,000° C., and becomes malleable when hot. Ruthenium combines with chlorine at a red heat, and is insoluble in acids, being scarcely attacked even by aqua regia.

COMPOUNDS OF RUTHENIUM

100. Three oxides of ruthenium are known. The sesquioxide, Ru_2O_3, is obtained as a blue powder insoluble in acids by heating the finely divided metal in the air. When metallic ruthenium is fused in an oxidizing atmosphere or the sulphate is roasted in the air, the dioxide, RuO_2, is obtained. It crystallizes in small pyramids, which are very hard, have a green, metallic luster, and a specific gravity of 7.2. The peroxide, RuO_4, is formed when ruthenium is heated to 1,000° C. in oxygen and is cooled rapidly, or by heating ruthenium with potassium nitrate and hydroxide and saturating the solution of the fused mass with chlorine. It is soluble in water, melts at 25.5° C., and decomposes without explosion at 107° C.

Ruthenium trichloride, $RuCl_3$, is formed when the metal is heated in a mixture of chlorine and carbon dioxide. It forms

orange-colored solutions which, on treatment with hydrogen sulphide, are changed to blue solutions of the dichloride, $RuCl_2$. Double chlorides, known as chlororuthenites, M_2RuCl_5, and chlororuthenates, M_2RuCl_6, exist. Sulphates corresponding with RuO and Ru_2O_3 have also been obtained.

RHODIUM

Symbol Rh. Atomic weight 102.9

101. Rhodium was discovered by Wollaston, who announced his discovery in 1804. He gave it the name of rhodium, from the rose color of the solution of rhodium salts. The metal and compounds were investigated by Berzelius and Claus. It is found in platinum ores and with some rare gold ores.

Rhodium is prepared by treating the solution from which the platinum has been precipitated with metallic iron, which precipitates the metals still in solution. This precipitate is fused with lead, and the lead, copper, and palladium dissolved out with nitric acid. The residue is digested with nitric acid and chlorine, or with aqua regia, converting the rhodium into the chloride, which is precipitated as the double ammonium chloride, is purified by repeated recrystallization, and ignited in the oxyhydrogen flame.

102. Rhodium forms a hard, white metal of the color and luster of aluminum. It has a specific gravity of 12.1, is more difficult to melt than platinum, melting at 1,970° C., and is nearly as ductile as silver. Rhodium is unaltered in the air at ordinary temperatures, but oxidizes at a red heat. When solidifying after melting it spits like silver, the surface becoming blue from oxidization. It can be distilled at the temperature of the electric furnace. When the metal is precipitated from solutions of its salts by alcohol or formic acid, it is obtained as a spongy, black powder. Pure rhodium is practically insoluble in all the acids, singly or together. Alloyed with zinc, lead, or copper, it is soluble in aqua regia. This is

also true of alloys of platinum and rhodium containing small amounts of rhodium. On the other hand, it does not dissolve in aqua regia, when alloyed with gold or silver. Rhodium can be dissolved by repeatedly fusing it with potassium bisulphate or with acid phosphates. Chlorine readily attacks rhodium.

RHODIUM COMPOUNDS

103. Rhodium forms a monoxide, RhO; a dioxide, RhO_2; and a sesquioxide, Rh_2O_3. Only one chloride, the trichloride, $RhCl_3$, is known. Rhodium burns in sulphur, forming the monosulphide, RhS; a sesquisulphide, Rh_2S_3, is obtained when hydrogen sulphide is passed over hot solutions of rhodium salts. A yellow crystalline sulphate, $Rh_2(SO_4)_3 \cdot 12H_2O$, with a sour astringent taste is obtained when the hydrated hydroxide, having the formula $Rh(OH)_3 \cdot H_2O$, is dissolved in sulphuric acid.

PALLADIUM

Symbol Pd. Atomic weight 106.7

104. Palladium was discovered at the same time as rhodium by Wollaston. It occurs associated with platinum and alloyed with native gold. When alloyed with gold the palladium is obtained by fusing the alloy with silver, dissolving the silver and palladium in nitric acid, precipitating the silver with sodium chloride, filtering, and throwing the palladium out of the filtrate with metallic zinc. Palladium is distinguished from platinum by the fact that palladium forms an insoluble cyanide. This fact is frequently taken advantage of in the preparation of the metal. Mercuric cyanide is added to a solution containing palladium, precipitating the cyanide, which is then ignited and yields spongy palladium.

105. Palladium is a hard, silver-white metal having a specific gravity of 11.4, and melting at 1,550° C. It is malleable and ductile. When heated to a dark red it assumes a green to violet tint. It is only slightly tarnished in the air, but at a red heat it becomes coated with the oxide. It is slowly soluble in nitric acid.

Palladium is remarkable for its power of absorbing hydrogen in large quantities. It occludes hydrogen even at ordinary temperature, but if heated to 100° C. in hydrogen it takes up over 960 times its own volume of the gas, and its specific gravity is materially decreased. If the temperature is increased it begins to give off hydrogen at 130° C. It has been suggested that a compound or alloy having the composition Pd_2H is formed; some indications favor this view, but it can hardly be considered as proved at present.

106. Palladium forms two classes of compounds; namely, the palladious compounds, in which this metal is bivalent, and the palladic compounds, in which it is quadrivalent. It is useful, on account of its hardness, lightness, and resistance to tarnish, in the construction of scientific instruments; alloyed with silver, it is used for small weights. It forms three oxides, Pd_2O, PdO, and PdO_2, and two chlorides, $PdCl_2$ and $PdCl_4$.

OSMIUM

Symbol Os. Atomic weight 190.9

107. History and Occurrence.—Osmium is always present in the residue from platinum ores in combination with iridium. In 1804 Tennant showed that the platinum residues contained the two new metals iridium and osmium, the latter so named from the Greek word meaning a *smell*, because of the peculiar odor of the peroxide. Osmium occurs in the platinum ores as an alloy of iridosmium.

108. Preparation.—Osmium is easily separated from the platinum residues by heating them in a porcelain tube through which a current of air is passed, converting the osmium into the volatile peroxide. This is then mixed with carbon monoxide and passed through a red-hot porcelain tube, when the metal is obtained in the form of a powder. By fusing the powder with tin in a graphite crucible, treating the alloy formed with hydrochloric acid, and heating the residue in a current of hydrochloric-acid gas, the crystalline variety is obtained.

109. Properties.—Osmium is a bluish-white metal, harder than glass, and has a specific gravity of 22.48. It is almost infusible in the absence of air, but when strongly heated in the air it burns with the formation of the poisonous peroxide. Because of its high melting point, about 2,700° C., osmium is used for the manufacture of incandescent electric lamps and, alloyed with iridium, for the tips of gold pens.

110. Osmium Compounds.—Five oxides of osmium are known: the monoxide, OsO, a gray-black powder insoluble in acids; the sesquioxide, Os_2O_3, also black and insoluble in acids; the trioxide, OsO_3; the dioxide, OsO_2, which forms a copper-colored mass which decomposes in the air; and the extremely poisonous peroxide, OsO_4, which forms colorless prismatic crystals that volatilize below the boiling point of water and have an irritating vapor that affects the eyes and stains the skin black. The oxides OsO, Os_2O_3, and OsO_2 are bases; OsO_3 unites with the bases, forming salts called osmites, M_2OsO_4; and OsO_4 acts as an indifferent oxide.

Osmium dichloride, $OsCl_2$, and osmium tetrachloride, $OsCl_4$, are obtained as two distinct bodies when the metal is heated in chlorine; $OsCl_2$ is the less volatile and forms green, needle-like crystals, while $OsCl_4$ is a dark-red powder.

IRIDIUM

Symbol Ir. Atomic weight 193.1

111. Occurrence and Preparation.—When Tennant discovered osmium and iridium in the residues from platinum ore he found that the salts of the one metal had different colors and to this metal he gave the name iridium. It is found in platinum ores alloyed with platinum and with osmium. The platinum-iridium alloy is found in the form of small cubes, whereas the osmium-iridium alloy occurs as irregular, flat grains. Iridium is prepared from the latter alloy by fusing with zinc and heating until the zinc is all driven off. The residue is then ignited with barium nitrate, the mass leached with water and boiled with nitric acid. The iridium is then pre-

cipitated as ammonium-iridium chloride and ignited, yielding spongy iridium. This is purified by fusing with lead and treating the resulting mass with nitric acid and with aqua regia.

112. Properties.—Iridium is a white, steel-like metal with a specific gravity of 22.4. Next to osmium and ruthenium, it is the most difficult metal of the platinum group to fuse, and is the least volatile of this group. It melts at about 2,000° C., is very brittle when cold, but somewhat malleable at a white heat. It does not oxidize in the air. The pure metal, in the massive state, is insoluble in aqua regia. When alloyed with considerable platinum, however, it is acted upon. It unites with chlorine at a low red heat. Alloyed with platinum it forms a hard, elastic compound that takes a fine polish and does not tarnish.

113. Iridium Compounds.—Iridium sesquioxide, Ir_2O_3, is the product of the oxidation of finely divided iridium in the air. It is a black powder insoluble in acids, begins to decompose at 800° C., and at 1,000° C. is converted into the metal and oxygen. The dioxide, IrO_2, is a black powder obtained when the hydroxide is heated in a current of carbon dioxide. The tetrachloride, $IrCl_4$, is obtained when the finely divided metal (as opposed to massive) is dissolved in aqua regia. The dichloride, $IrCl_2$, is obtained by heating a solution of the tetrachloride or by passing the tetrachloride over finely divided iridium heated to a red heat. The trichloride, $IrCl_3$, is prepared by heating a double chloride with sulphuric acid.

PLATINUM

Symbol Pt. Atomic weight 195.2

114. History and Occurrence.—Platinum has been known for many centuries, but was first thoroughly investigated during the 18th century. It was first described by Watson in 1750 and more exactly by Scheffer in 1752, who described it as white gold. It derives its name from the Spanish *platina,* meaning little silver. It is found in nature in

the metallic state in flattened grains in river sands. It is never pure, being always accompanied by the metals of this group, together with some iron, copper, and gold. The principal source of supply is the Ural Mountains of Russia, though it is also found in Brazil, Peru, Borneo, Australia, and California.

115. Preparation.—Platinum is usually prepared by wet methods. The ore is treated with aqua regia until all of the platinum is dissolved; the solution is then filtered. The filtrate is treated with lime water until only slightly acid, thus removing the iron, copper, iridium, rhodium, and part of the palladium. The filtrate is evaporated to dryness, ignited, and then washed with dilute hydrochloric acid. The platinum thus obtained is fused with lead, and digested with nitric acid, removing any lead, copper, and other impurities. The residue is dissolved in aqua regia and the platinum precipitated with ammonium chloride. As the precipitate contains some rhodium, it is fused with potassium bisulphate, leached with water to dissolve the rhodium sulphate formed, the precipitated platinum heated to redness, and then fused into a compact form before the oxyhydrogen blowpipe.

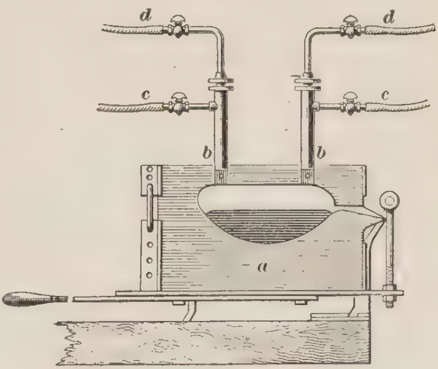


FIG. 7

116. Today most large manufacturers of platinum ware fuse the metal in a furnace developed by Deville and Debray. This furnace is illustrated by Fig. 7. It consists of a large, hollowed-out block of quicklime *a*, equipped with two burners *b* to which are fed coal gas and oxygen, the former passing through *c* and the latter through *d*. Lime is used in the construction of this furnace because it will stand a high temperature and at the same time it will remove impurities such as silicon, if present in the platinum.

117. Properties.—Pure platinum is a tin-white metal softer than silver, but is hardened by the presence of other metals, especially iridium. It has a specific gravity of 21.16, melts at 1,753° C., and can be welded at a white heat. Owing to its low coefficient of expansion, which is very nearly the same as that of glass, it can be sealed into glass without cracking the latter by unequal contraction on cooling. It is not affected by the air, is insoluble in all single acids, but alloys readily with phosphorus, silver, lead, tin, bismuth, arsenic, antimony, etc. It absorbs hydrogen at a red heat and also causes many bodies to combine with oxygen.

Its resistance to the action of acids and to high temperatures renders platinum very valuable in chemical processes. It is indispensable to the analytical chemist. It can be easily rolled into thin foil and drawn into fine wires, it having been drawn into a wire $\frac{1}{30000}$ inch in diameter.

118. Platinum, as has already been stated, possesses the power of inducing chemical combination between oxygen and other gases to a remarkable degree. The spongy as well as the compact metal possesses this property. This can be readily shown by heating a piece of platinum foil to redness in a Bunsen burner, extinguishing the gas, and rapidly turning it on again, when the cold gas will keep the foil at a red heat, in consequence of the combination with atmospheric oxygen at the surface of the platinum.

Spongy platinum in a very active form is obtained by gently igniting ammonium platinic chloride. This forms a porous mass of finely divided metallic platinum which has an extremely large surface compared with its mass.

119. Platinum Black.—When platinum is precipitated in the metallic state from its solutions to which other metals have been added, it forms a soft, black powder known as platinum black.

$$PtCl_4+2Zn=Pt+2ZnCl_2$$

This substance has the power of absorbing more than 800 times its volume of oxygen. This oxygen does not combine with the platinum, but is condensed into its pores, and is avail-

able for combination with other substances. The power of promoting combination with oxygen is so great that if it is introduced into hydrogen, the oxygen will at once unite with hydrogen and form water. After being heated to redness for a number of times platinum black becomes denser and loses considerable of its activity.

COMPOUNDS OF PLATINUM

120. Oxides of Platinum.—Two oxides of platinum are known. Platinous oxide, PtO, prepared by the ignition of the corresponding hydroxide, $Pt(OH)_2$, is a gray or violet powder that is converted into the metal when strongly heated. When heated with a solution of formic acid, a violent evolution of carbon dioxide occurs and platinum black is formed. Platinic oxide, PtO_2, is obtained in a similar manner. Platinic hydroxide, $Pt(OH)_4$, and platinous hydroxide, $Pt(OH)_2$, are obtained by treating the corresponding chlorides with sodium hydroxide. The former is acid in character and forms a few salts of the formula $M_2Pt(OH)_6$; the latter is an oxidizing agent and acts as a weak base.

121. Chlorides of Platinum.—The most important and best known salt of platinum is platinic chloride, $PtCl_4$. This may be prepared by heating metallic platinum in chlorine to a temperature of about 1,300° C. It may also be prepared by dissolving scrap platinum in a mixture of 4 volumes of hydrochloric acid and 1 volume of nitric acid, gently evaporating the solution to a syrupy consistency, redissolving it in hydrochloric acid, and again evaporating the solution to a syrup.

The evaporation must not be carried on too rapidly or too far, because of the possibility of forming some metallic platinum. On cooling, the liquid solidifies to a red-brown mass very soluble in water and alcohol, and absorbs moisture from the air. If the solution is allowed to crystallize before all the hydrochloric acid is expelled, brown, prismatic needles of chloroplatinic acid, $H_2PtCl_6{\cdot}6H_2O$, are obtained. This acid forms chloroplatinates by the replacement of its hydrogen by

metals. With the alkali metals it forms salts that, owing to their great differences in solubility, are very valuable to the analytical chemist.

Potassium chloroplatinate, K_2PtCl_6, or potassium platinic chloride, is precipitated as a yellow crystalline mass when a solution of potassium chloride is added to a solution of chloroplatinic acid. It is slightly soluble in hot water, 5 parts in 100 parts of water, and is insoluble in alcohol.

Sodium chloroplatinate, Na_2PtCl_6, is obtained in the form of red prisms or tablets and differs from the potassium salt in being readily soluble in water and alcohol.

Ammonium chloroplatinate, $(NH_4)_2PtCl_6$, is obtained as a lemon-yellow crystalline mass when chloroplatinic acid is added to an ammonium salt. It is sparingly soluble in water and insoluble in alcohol. When heated it decomposes without fusion, yielding spongy platinum.

Platinous chloride, $PtCl_2$, is prepared by heating chloroplatinic acid to 300° C., when chlorine is evolved. It is also prepared by heating spongy platinum in a current of dry chlorine to 250° C. It forms a dingy-green powder insoluble in water or in nitric or sulphuric acid. It is soluble in hot hydrochloric acid, yielding a red solution. Heat decomposes it into chlorine and platinum. The hydrochloric-acid solution, when added to ammonium chloride, yields a double salt, ammonium chloroplatinite, $(NH_4)_2PtCl_4$. The potassium salt, K_2PtCl_4, forms rose-colored, crystalline fibers, and forms the starting point for the formation of chloroplatinous acid, H_2PtCl_4, and its salts.

122. Iodides of Platinum.—Platinic iodide, PtI_4, is a dark-brown to black amorphous substance obtained when hydriodic acid acts on a soluble chloroplatinate. It is soluble in hydriodic acid, forming the soluble, unstable compound iodoplatinic acid, $H_2PtI_6 \cdot 9H_2O$. Platinous iodide, PtI_2, is formed as a black powder when platinous chloride and potassium iodide are boiled together.

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NOTE.—In this volume, each Section is complete in itself and has a number. This number is printed at the top of every page of the Section in the headline opposite the page number, and to distinguish the Section number from the page number, the Section number is preceded by a section mark (§). In order to find a reference, glance along the inside edges of the headlines until the desired Section number is found, then along the page numbers of that Section until the desired page is found. Thus, to find the reference "Acid salt, §8, p49," turn to the section marked §8, then to page 49 of that Section.